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Comparison of Automated and Manual Sulfuric Acid Sampling Systems

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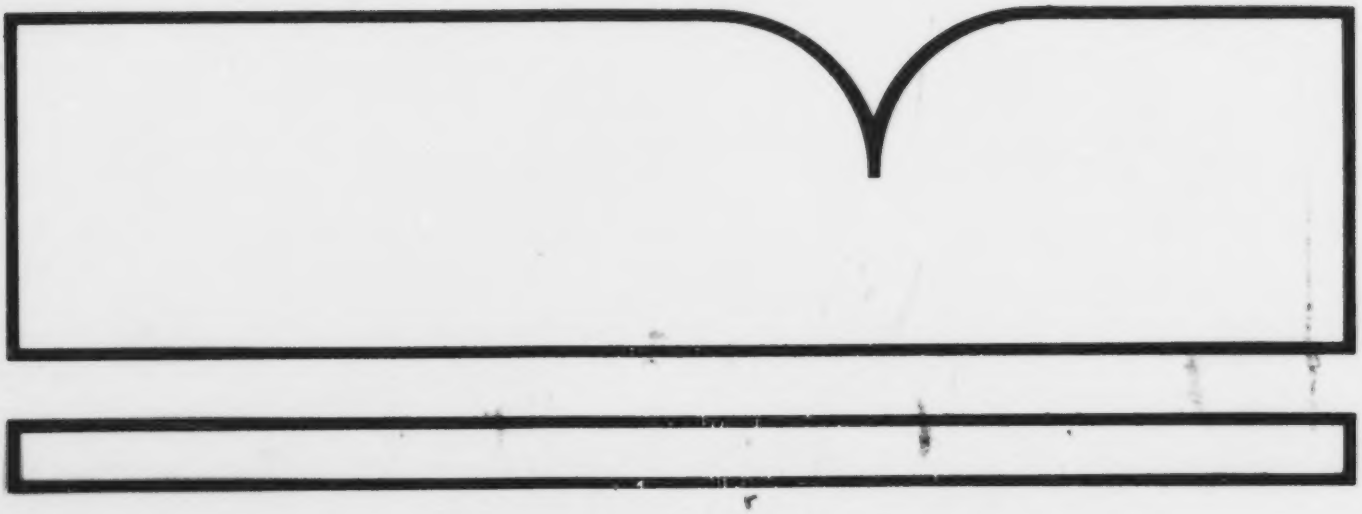

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COMPARISON OF AUTOMATED AND MANUAL SULFURIC ACID SAMPLING SYSTEMS

by

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The purpose of this program was to evaluate the performance of three sulfuric acid vapor sampling systems consisting of (1) a commercially available continuous monitor (SSL) manufactured by Severn Science Limited of Great Britain, (2) an automated prototype sulfuric acid mist monitor (SAMM) developed by the U.S. Environmental Protection Agency, and (3) a miniaturized, manually controlled-condensation system, also developed by EPA.

During the initial phase of the program, the operational characteristics of each system were determined in the laboratory with a thermal generator as a source of sulfuric acid vapor. The same systems were then evaluated at the inlet and outlet of an electrostatic precipitator during a 10-day field test at the coal-fired Johnsonville Steam Plant of the Tennessee Valley Authority.

During the laboratory determinations good agreement was obtained among the three samples over a sulfuric acid concentration range of 2 to 20 ppm. During the field testing, the inlet sampling results showed average sulfuric acid concentrations of 12, 12, and 10 ppm for the SSL, SAMM, and manual method, respectively. At the outlet the same systems gave 4, 4, and 3 ppm concentrations, respectively, of sulfuric acid. Difficulties were experienced which included unexpectedly large variations in the SSL results and major operational problems with the prototype SAMM.

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ABSTRACT

The purpose of this program was to evaluate the performance of three sulfuric acid vapor sampling systems consisting of (1) a commercially available continuous monitor (SSL) manufactured by Severn Science Limited of Great Britain, (2) an automated prototype sulfuric acid mist monitor (SAMM)* developed by the U.S. Environmental Protection Agency (EPA) and (3) a miniaturized, manual controlled-condensation system, also developed by the EPA. We determined the operational characteristics of each system in the laboratory using a thermal generator as a source of sulfuric acid vapor. Comparison of the responses of the automated systems to the manual system showed the automated samplers to be within 10% of the manual system over a sulfuric acid concentration range of 2 to 20 ppm.

We also evaluated the same systems at the inlet and outlet of an electrostatic precipitator at a coal-fired power plant. At the inlet sampling location, average sulfuric acid concentrations were 12, 12, and 10 ppm, as determined by the SSL, the SAMM, and the manual system, respectively. At the outlet location, these systems gave average sulfuric acid concentrations of 4, 4, and 3 ppm, respectively.

We experienced relatively few operational problems with the SSL during this study. The system was compact, flexible, and simple to operate. Although the SSL was in general agreement with the SAMM and manual systems during this field evaluation, the transient, positive excursions observed with this monitor, but not with the other systems, were a cause of concern and should be investigated further. The SAMM, in its present state of development, is an awkward system and would require major modifications in size and complexity before it could be used in routine field applications. No specific recommendations for modification of the manual system appear to be warranted.

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*The name of this monitor is actually a misnomer because the device is designed to <u>reject</u> sulfuric acid and collect only the vapor.

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Section 1

INTRODUCTION

Sulfuric acid in the flue gas of coal- and oil-fired power plants has long been a matter of concern to the utilities industry because of its corrosive attack on plant equipment as well as its adverse effect on the surrounding environment. The accurate determination of low concentrations (parts per million) of this acid in the presence of particulate matter, water vapor, and sulfur dioxide, however, has not been without problems. Considerable progress has now been made, nevertheless, in the development of adequate measurement techniques based primarily on the selective condensation of sulfuric acid in a temperature-controlled device, after particulate matter removal. This approach has been used in manual systems and in a prototype monitor (SAMM) developed under an EPA contract. Another monitor (SSL), designed to monitor continuously the sulfuric acid concentration in flue gases, has recently been made commercially available by Severn Science Limited of Great Britain.

The purpose of this contract was to evaluate the performance of the EPA prototype system, the Severn Science Limited system, and a manual controlled-condensation system, both in the laboratory and at the inlet and outlet of an electrostatic precipitator at a coal-fired power plant.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The three sulfuric acid sampling systems evaluated under the contract showed excellent agreement when exposed to known concentrations (2 to 20 ppm) of sulfuric acid vapor in the laboratory. The same degree of reproducibility was not obtained, however, in the field evaluation of these systems at sulfuric acid concentrations around 10 to 12 ppm or 3 to 5 ppm. The SSL, during periods of apparently stable plant operating conditions, oftentimes showed significant positive excursions above a more nearly constant response. As a rule, these excursions were not observed with the other systems; thus, the occasional excursions may have been artifacts rather than true indications of transient changes in the sulfuric acid concentration. No unequivocal confirmation of this assumption, however, was provided by the other available field test data.

From an operational viewpoint, the only problem experienced with the SSL was the need for rather frequent adjustments in the flow rate of isopropanol, which carries the collected sample to the colorimetric measurement cell. Otherwise, the monitor was found to be compact, simple to operate, and, because of the flexibility imparted by the umbilical line, adaptable for sampling in a variety of locations without the need for platforms or scaffolding.

Laboratory data obtained with the SAMM showed that instrument to be capable of detecting sulfuric acid vapor with a satisfactory degree of reproducibility once equilibrium had been attained. The relative standard deviation (RSD) for this system was about 10% at sulfuric acid concentrations of 5 to 15 ppm. During the field evaluation, the SAAM, when operational, produced results that were in general agreement with those obtained from the other systems.

We encountered considerable problems with the SAMM, both in the laboratory and in the field. The major cause of concern in the laboratory was the frequency at which leaks in the gas sampling system occurred. These same problems were experienced in the field, in addition to those of a more serious nature, such as failure of the refrigeration system and the mass flow controller. The instrument was bulky, heavy, and required rather precise positioning on a scaffold in order to align the system with the sampling probe. Extreme care in handling was necessary because of the intricate glassware incorporated into the unit. Although designed for unattended operation, essentially full-time attention was required to keep it operating properly during the field test program.

The reproducibility of the manual system with sulfuric acid vapor from the laboratory generator was considered to be very good, with an RSD of less than 5% at the 10 to 20 ppm H_2SO_4 level and less than 10% at the 2 to 4 ppm level. In the field, this system generally indicated somewhat lower sulfuric acid concentrations than did the two automated monitors.

The manual (controlled-condensation) system was operated without incident over the entire test program. Miniaturization of many of the components of this unit allowed the system to be transported and assembled with a minimum of effort. One potential disadvantage of this miniaturized system, however, is the limitation in sampling flow rates imposed by the use of midget bubblers and, possibly, small glass-wool condensers. At locations where sulfuric acid concentrations of 1 ppm or less might be encountered, long sampling time would be required to obtain sufficient acid for on-site analyses.

In summary, the sulfuric acid sampling systems were in general agreement when average, rather than single-point, values were used for comparison. The SSL monitor proved to be a compact, flexible unit, remarkably free from mechanical defects. The possibility of artifact responses from the SSL, however, should be thoroughly investigated at several test sites differing both in sulfuric acid concentration and fly ash composition. The SAMM in its present configuration is an awkward system not suitable for routine field sampling. A major reduction in size and overall complexity of this unit appears to be an absolute necessity. No specific recommendations for modification of the manual system are warranted.

SECTION 3

DESCRIPTION OF SAMPLING SYSTEMS

SULFURIC ACID MIST MONITOR (SAMM)

The prototype SAMM has been described in detail in previous publications.[1,2] Basically, the instrument selectively condenses sulfuric acid (H_2SO_4) vapor from sample streams, after removal of particulate matter by an electrostatic precipitator (ESP) that is incorporated in the sampling device, rinses the collected H_2SO_4 into a conductivity cell with a known volume of an isopropanol/water solution, and then measures the electrical conductance of the solution.

A timing board, covering a range of 1 to 999 s, allows the selection of an appropriate sampling cycle; therefore, the amount of H_2SO_4 collected during each cycle can be controlled to obtain concentrations compatible with the calibration curve. Figure 1 presents a schematic view of the overall system, whereas Figure 2 shows, in detail, the collection and detection system. The prototype electrostatic precipitator used for particulate matter removal is shown in Figure 3. To complete the sampling system, a temperature-controlled, 1.2-m, quartz-lined probe extracts flue gas samples from the sample duct.

SEVERN SCIENCE LIMITED MONITOR (SSL)*

This monitor was developed by the Central Electricity Generating Board (CEGB) of Great Britain for continuous monitoring of H_2SO_4 vapor over a concentration range from 1 to 50 ppm. The use of the isopropanol/water solution minimizes the collection of SO_2 as H_2SO_4 and also reduces the solubility of the barium chloranilate contained in the reaction bed. The sulfate in solution passes through this static, porous bed of barium chloranilate, where the following reaction occurs:

$$SO_4^{=} + BaC_6O_4Cl_2 + H^+ \longrightarrow BaSO_4 + HC_6O_4Cl_2^-$$

The absorbance of the chloranilate ions in the effluent from the reaction bed is measured at 535 nm in a continuous flow-through photometer system, and the equivalent H_2SO_4 concentration is recorded on a strip chart recorder.

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*The specific instrument used in this investigation was leased from the Rolfite Company of Stanford, Connecticut.

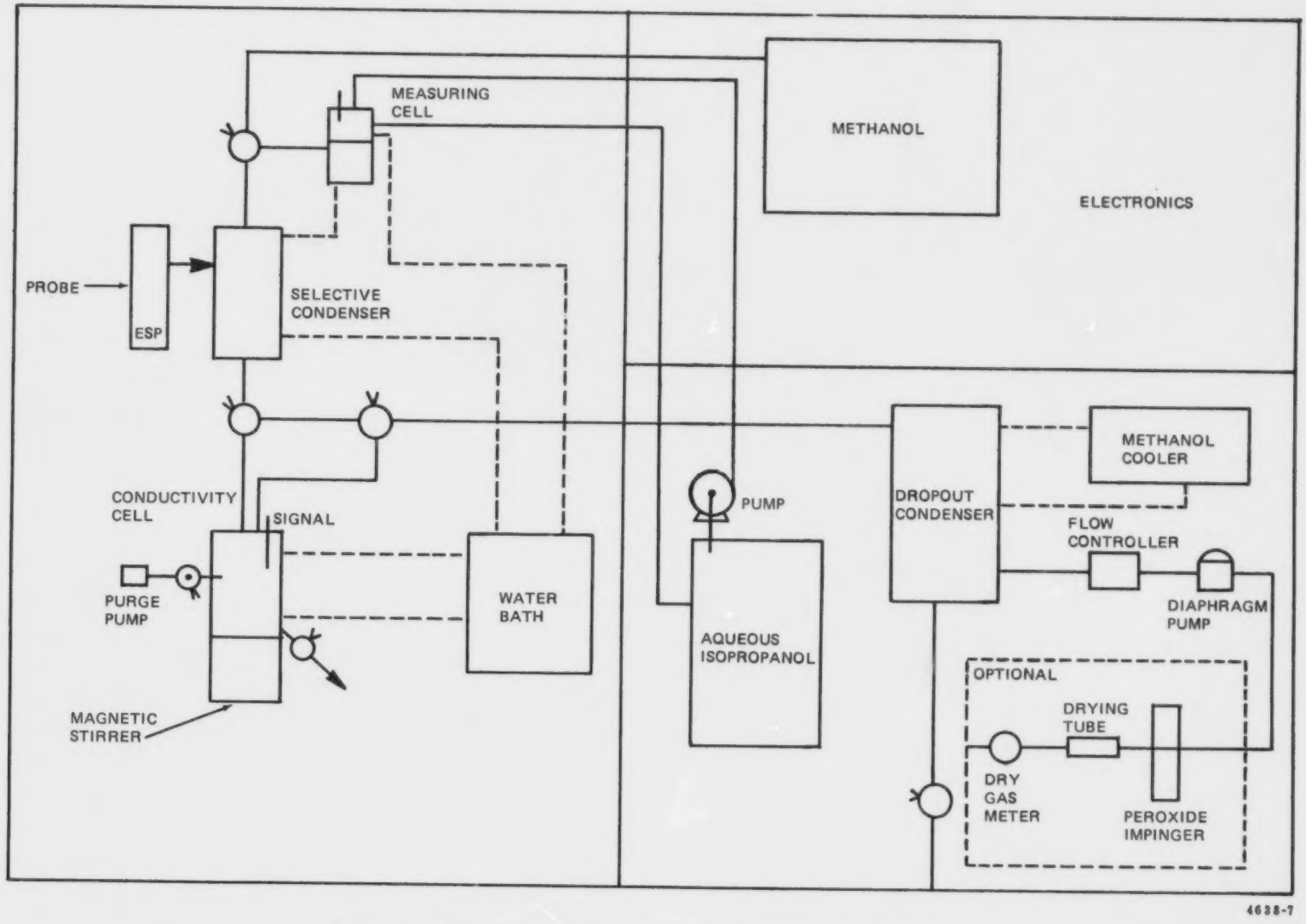

Figure 1. Schematic of the prototype sulfuric acid mist monitor.

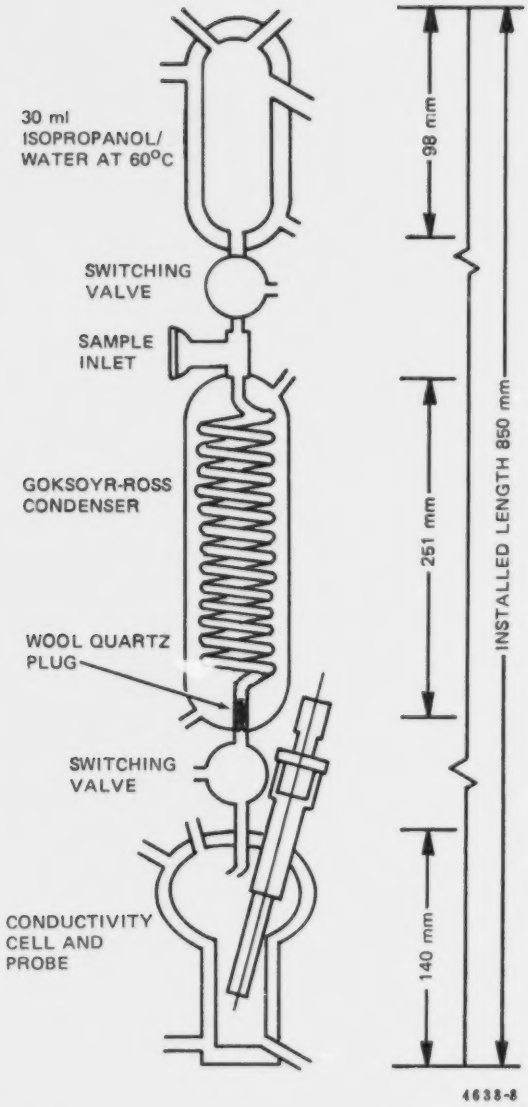

Figure 2. Collection and detection system for the sulfuric acid mist monitor.

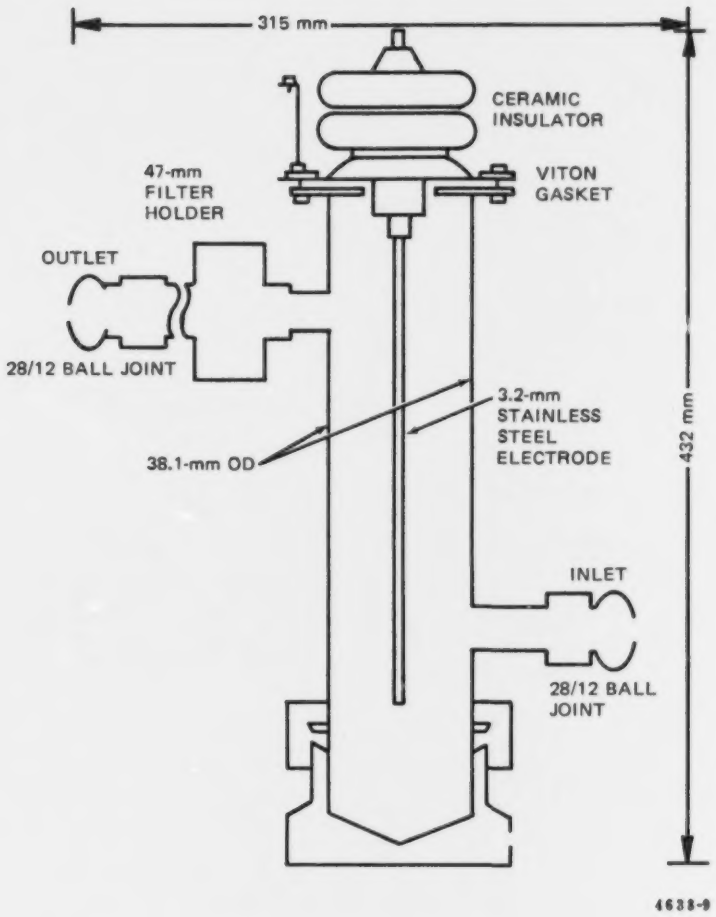

Figure 3. Prototype electrostatic precipitator.

With a constant ratio of flow rate of gas sample to flow rate of absorbing solution maintained, the concentration of sulfate in the isopropanol/water solution is made directly proportional to the concentration of H_2SO_4 in the sample stream. According to the manufacturer, the overall monitor accuracy is approximately $\pm$5% of the chart reading. The detection system of this instrument is based on the colorimetric determination of the acid chloranilate ion generated by the reaction of sulfate with barium chloranilate.[3,4]

As shown in Figure 4, the H_2SO_4 vapor is absorbed in a 4:1 isopropanol/water solution in the umbilical line between the heated quartz-wool particulate filter and the No. 4 sintered glass absorber. Any acid aerosol is coalesced with the bulk of the solution as it passes through the absorber.

Oxidation of SO_2 to H_2SO_4 in the SSL system is reported to be insignificant.[5] Using reagent-grade isopropanol, oxidation of 2000 ppm of SO_2 resulted in H_2SO_4 levels no greater than 0.3 ppm. Each batch of isopropanol, however, should be tested for oxidants by means of a potassium iodide procedure.[6]

The major SSL interferent likely to be encountered in the flue gas from coal-fired power plants is hydrogen chloride (HCl).[5] Absorption of HCl in the isopropanol solution results in an increase in the hydrogen ion concentration, which, in turn, depresses the absorbance of the acid chloranilate ion, but increases the solubility of barium chloranilate. The effect of 100 ppm of HCl on the SSL indicates that the error in the H_2SO_4 measurement should be no greater than $\pm$5% at H_2SO_4 levels between 2 and 20 ppm. Since the chlorine content of most coals is usually less than 0.1% (equivalent to about 60 ppm of HCl in the flue gas), interference from HCl would be minimal in all but exceptional cases.

MANUAL SAMPLING SYSTEM

The EPA-provided sampling system shown in Figure 5 is a miniaturized version of a manual system described elsewhere.[7] The system consists of, in sequence, a 0.85-m heated probe with quartz liner, a quartz filter holder fabricated from a 28/12 ball-and-socket joint, a temperature-controlled condenser packed with Pyrex wool, and a series of three midget impingers followed by a Drierite tower, a leak-free pump, a flowmeter, and a dry gas meter.

During operation, the probe and filter are maintained at 270 °C; the condenser at 65 °C. The H_2SO_4 vapor is collected in the condenser; the SO_2 is collected in a 3% solution of hydrogen peroxide in the impingers. The H_2SO_4 is recovered by flushing the condenser first with 10 mL of deionized water and then with 40 mL of pure isopropanol. The SO_2 impingers are combined into a single sample and diluted to an appropriate volume.

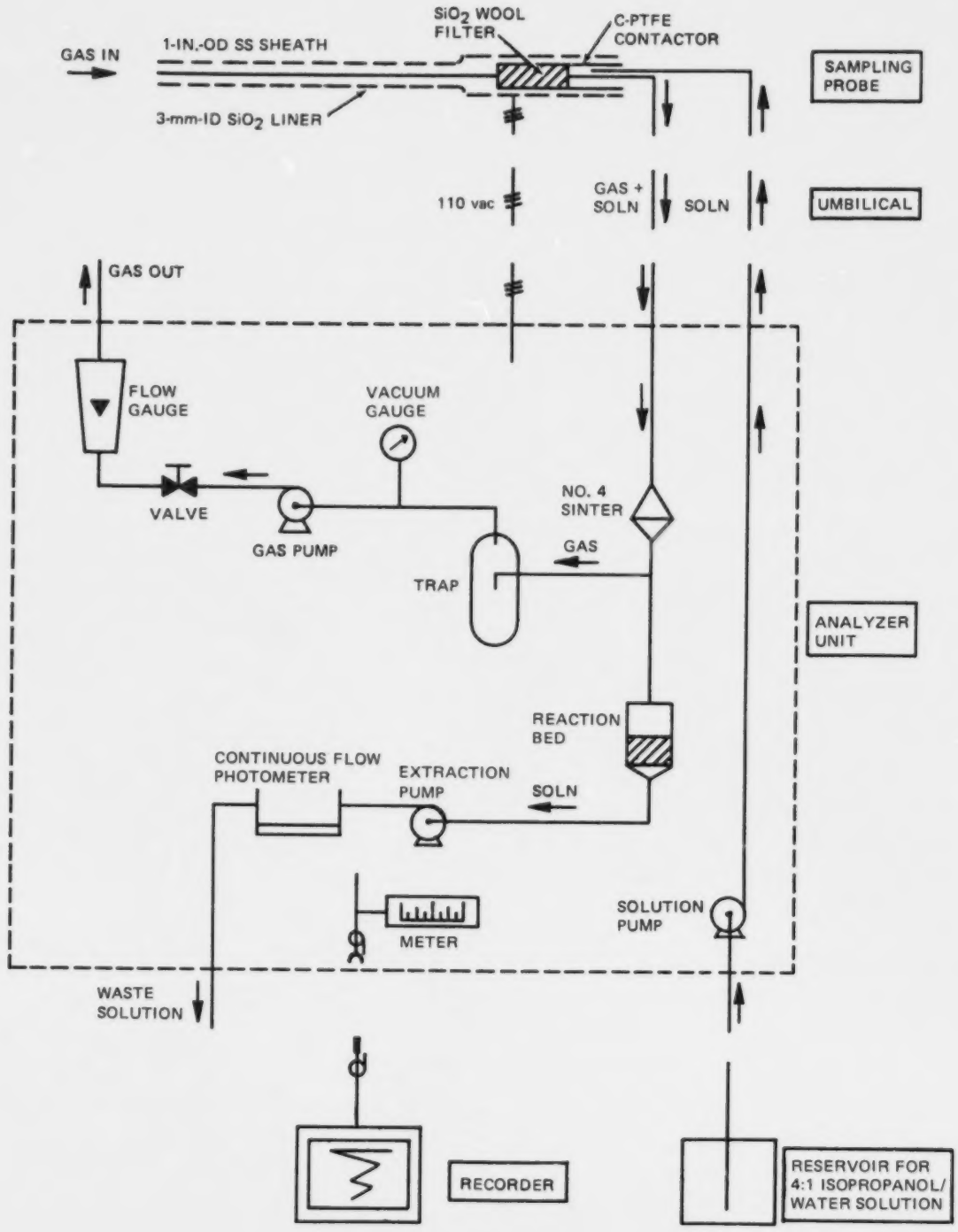

Figure 4. Schematic diagram of the SSL monitor.

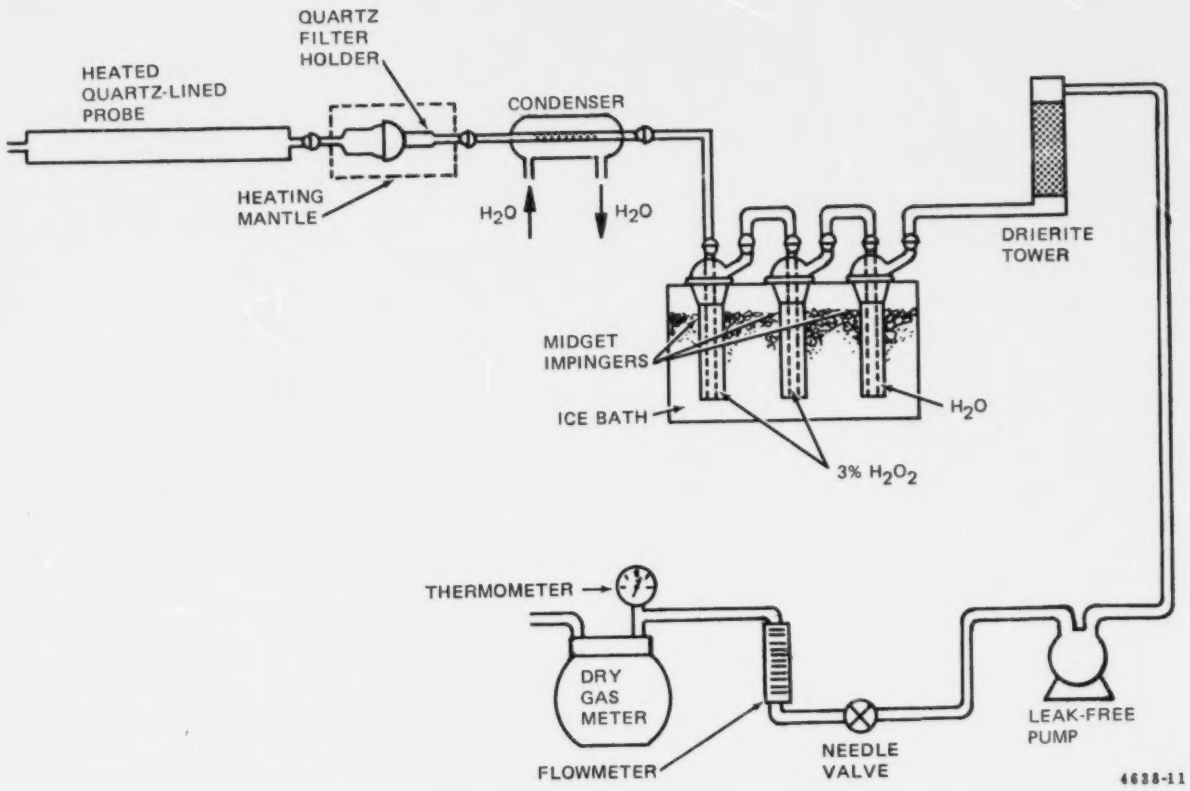

Figure 5. Manual SO_X sampling system.

The sulfate content of the samples is determined by titration with a standard solution of barium perchlorate using thorin as an end-point indicator.[8,9,10] A number of cations and anions are reported to interfere with this procedure.[9,10] Since the majority of these interferents are associated with the fly ash, the quartz filter used for the removal of particulate matter would be expected to eliminate this potential source of error. Therefore, only the vapor-phase components of the flue gas would come in contact with the H_2SO_4 condenser. One anion that has a significant effect on the sulfate analysis is fluoride. The hydrogen fluoride concentration in the flue gas should be insignificant, however, so no interference problems would be anticipated, even if the hydrogen fluoride were efficiently collected in the condenser.

Examples of the methods used in the calculation of sulfuric acid, sulfur dioxide, and sulfate concentrations are given in Appendix B.

SECTION 4

LABORATORY COMPARISON OF THE AUTOMATED SAMPLING SYSTEMS WITH THE MANUAL SYSTEM

SULFURIC ACID VAPOR GENERATOR

A generator capable of producing H_2SO_4 vapor concentrations from about 2 to 20 ppm was assembled to assess the performance of the sampling systems in the laboratory. The generator shown in Figure 6 consisted of a GTE Sylvania serpentine air heater, a Retec (Cavitron Corporation, Van Nuys, CA) or Puritan (Puritan-Bennett Corporation, Kansas City, MO) nebulizer for dispersing an aerosol of H_2SO_4 (subsequently volatilized), a humidifier, and an externally heated quartz tube fitted with sampling ports. Inlet air temperatures were maintained at about 360 °C; outlet gas temperatures at about 280 °C. Small changes in H_2SO_4 concentration could be obtained by varying air flow rates; larger changes, however, required a change in the strength of the solution being nebulized.

SULFURIC ACID MIST MONITOR (SAMM)

Operational Difficulties

We encountered three problem areas during the initial operation of SAMM: (1) the maximum sampling flow rate that could be attained was only about 12 L/min rather than the 50 L/min indicated in the instruction manual, (2) condensed methanol could not be drained from the chiller section because negative pressure developed in the SAMM when operated at maximum gas flow rates, and (3) plastic connectors were prone to air leaking in.

The quartz wool plug in the condenser was responsible for the limitation in flow; removal of this plug allowed the pumps to operate at approximately 32 L/min. Because the plug is necessary for the collection of any H_2SO_4 present in the condenser as an aerosol, however, the maximum sampling rate for the SAMM appeared to be limited to 12 L/min.

Attempts to drain methanol from the chiller were unsuccessful even when flow rates were reduced to 10 L/min. Therefore, a small vacuum pump was connected to the methanol drain line to overcome the negative systemic pressure and to allow the methanol to be removed during the vent cycle.

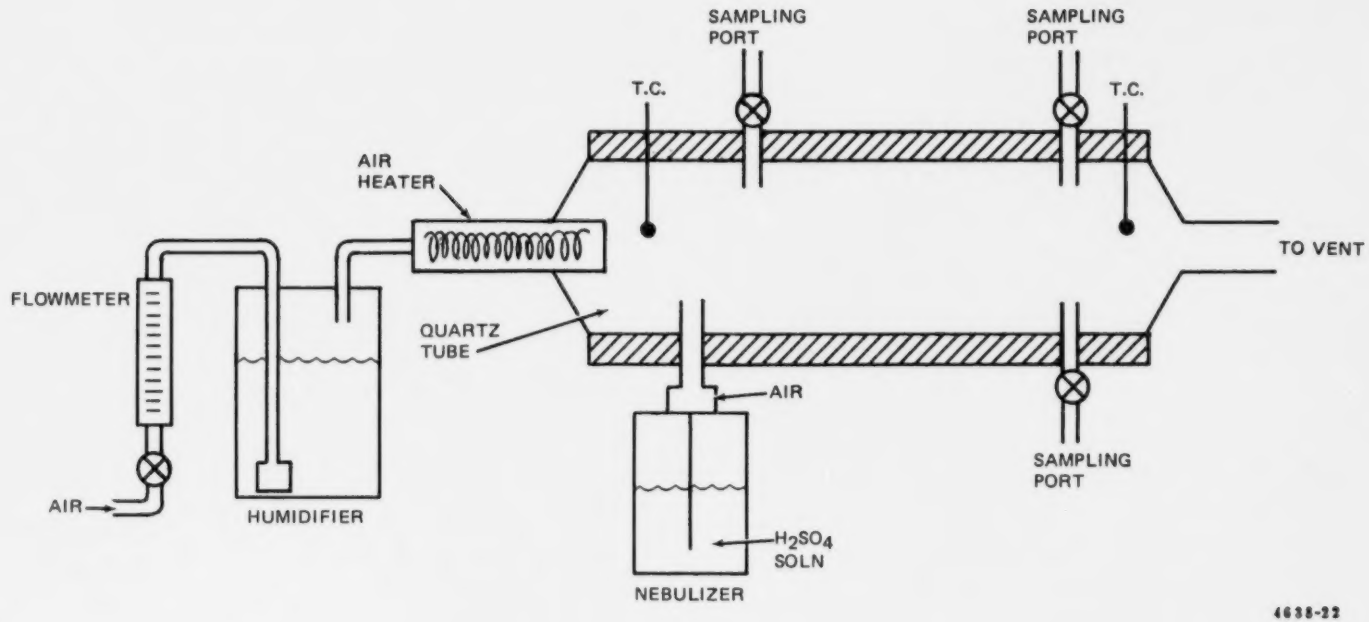

Figure 6. Sulfuric acid vapor generator.

Calibration

The volume of the isopropanol measuring cell and solenoid well was measured and found to be 35 mL. Standard solutions of H_2SO_4 in isopropanol were then prepared to give from 2 to 5 mg of H_2SO_4 in 35 mL of isopropanol. A calibration curve was obtained by adding 35-mL portions of standard solutions to the inlet of the condenser, draining the sample into the conductivity cell by appropriate use of the solenoid relays, and then reading the conductivity cell output. Curves were obtained for approximately equivalent concentrations of H_2SO_4 in solutions of 80%, 90%, and 95% isopropanol in water. As shown in Figure 7, an appreciable difference in the slopes of the curves was observed. Unless high H_2SO_4 concentrations are anticipated, the use of 80% isopropanol would seem most desirable because of the enhanced sensitivity in this medium.

Since recovery and manual titration of several SAMM samples were required during the field tests, the efficiency of sample recovery from the conductivity cell was determined. In the normal mode of operation, the sample is vented from the cell by means of an air pump. Considerable splashing occurs, making sample collection difficult. To circumvent this problem, the SAMM was switched to manual operation, the solenoids opened, and the sample extracted into a 60-mL container by means of a small vacuum pump. This procedure resulted in the complete removal of the sample from the cell under more closely controlled conditions.

Efficiency of Sample Recovery

To determine the efficiency of sample recovery, 35 mL of an H_2SO_4 standard was first introduced into the condenser, drained into the conductivity cell, and recovered as described above. The H_2SO_4 content of this sample, as determined by a barium perchlorate [$Ba(ClO_4)_2$] titration, was then compared to the H_2SO_4 content of a 35-mL aliquot of the standard solution. Four such tests resulted in an average recovery of only 78 $\pm$ 3%. A second series of tests, in which the condenser and cell were washed with 35 mL of isopropanol following a sample collection, resulted in a recovery efficiency of 95 $\pm$ 3%. Therefore, at least one rinse cycle was incorporated into the sample recovery procedure.

Response to the H_2SO_4 Vapor Generator

Next, the response of the SAMM to vapor from the H_2SO_4 generator was compared to the H_2SO_4 concentration determined by the manual system. Because of the size and weight of the SAMM and space limitations in the vicinity of the generator, a commercial heated sampling line, with a Teflon core, was used to mate the generator with the monitor. Good agreement between the SAMM and the manual system was obtained at two different H_2SO_4 concentrations. At the lower level, the SAMM indicated 2.5 ppm, the manual system 2.6 ppm; at the higher level, the SAMM indicated 14 ppm, the manual system 15 ppm.

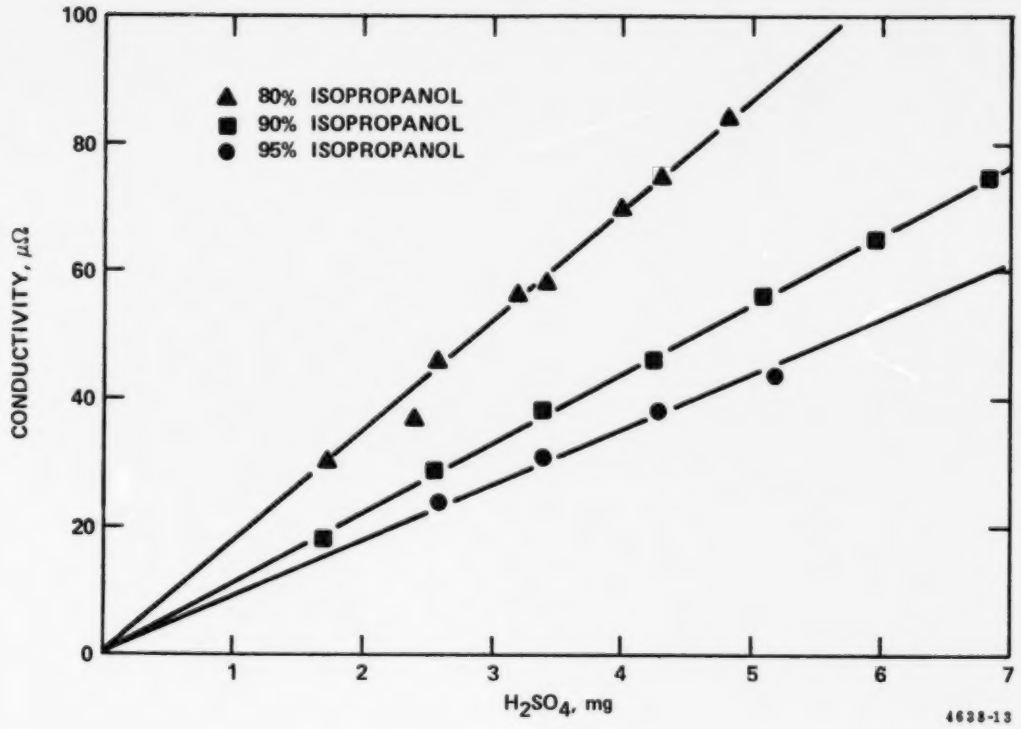

Figure 7. SAMM H_2SO_4 Calibration curve.

These tests with the SAMM were made without the ESP in line. Since the ESP could conceivably act as a sink for H_2SO_4, SAMM responses to 7 ppm of H_2SO_4 from the vapor generator were recorded with and without the ESP in the sampling system to determine whether any loss of acid could be observed. Only 10% of the original SAMM signal was obtained after the first cycle with the ESP in line. This response increased to 42% after 60 min and 74% after 120 min, and it was essentially 100% of the expected signal after 180 min of operation. A heating mantle was used to maintain the main body of the ESP at 235 °C during the test. The exposed inlet and outlet connections of the ESP were heat traced with heating tape to reduce the possibility of acid condensation in these areas.

A similar test was conducted on the following day without cleanup of the ESP from the previous test. As before, the SAMM response to approximately 6 ppm of H_2SO_4 vapor was found to increase with successive sampling cycles, reaching 68% of the expected response after 60 min of operation. Although the test was terminated at this point because of mechanical problems in the SAMM, the results appeared to indicate a more rapid approach toward equilibrium than observed in the initial test when a clean ESP was used.

Additional studies were then conducted to further evaluate H_2SO_4 holdup in the ESP. The SAMM response to H_2SO_4 from the vapor generator was first determined without the ESP in line. Next, the ESP, at 270 °C, was inserted into the sampling system, without cleanup from the previous tests, and the response was recorded until an equilibrium signal was obtained. During the initial test, approximately 20 min was required to reach equilibrium. During successive tests under similar conditions, no H_2SO_4 holdup in the ESP was observed. The ESP was then removed and thoroughly cleaned. During the first test following cleaning, about 60 min of sampling was needed to condition the ESP. Similar results were obtained the next day without further cleaning of the ESP. Removal of the ESP from the sampling line had no effect on the SAMM response; this observation indicated that no H_2SO_4 holdup occurred in the ESP once equilibrium had been attained. The results also suggested that daily cleaning of the ESP during a field test should be avoided, if possible, in order to minimize the holdup problem.

During the laboratory evaluation, considerable difficulty was experienced with leaking in of air around the numerous plastic connectors, even at flow rates of 10 L/min. This leakage was due, in part, to the negative pressure developed between the quartz wool plug in the condenser and the air sampling pump and to the tendency of the connectors to loosen during operation. In many instances, substitution of a more rigid tubing was beneficial in reducing the leakage while eliminating the problem of tubing collapse in the vicinity of the internal heaters. Nevertheless, a significant amount of time was required during day-to-day operation to maintain a satisfactorily low leak rate in the SAMM.

SEVERN SCIENCE LIMITED MONITOR

Initial experiments with the SSL monitor showed that all components of the system, with the exception of a faulty recorder, were operational. Calibration curves obtained with known concentrations of H_2SO_4 in 4:1 isopropanol/water solution flowing through the SSL at 2.0 mL/min were reproducible from day to day and, as shown in Figure 8, were in good agreement with the curve supplied by the Rolfite Company.

Later, the probe and umbilical line were connected to the SSL for sampling of the H_2SO_4 vapor generator. At a generator concentration of 4 ppm, the SSL gave a response of only 2 ppm after the recommended 20- to 30-min equilibration time. A sample of solution, collected immediately upstream of the barium chloranilate bed, was titrated with $Ba(ClO_4)_2$. The analysis of this sample indicated a generator output of 3.6 ppm, or essentially complete recovery of the H_2SO_4. Analysis of the probe and filter confirmed that no H_2SO_4 was being held up in that part of the system. The generator output was then increased to 11 ppm of H_2SO_4. An SSL response of 10 ppm was considered to be in good agreement with the generator. A repetition of the tests at a reduced H_2SO_4 concentration resulted in an SSL response of 5.0 ppm as compared to a value of 5.5 ppm obtained by the manual method. The reason for the discrepancy between the SSL and the generator at the 4 ppm level was not resolved.

We encountered relatively few problems with the SSL. On one occasion, a significant base-line drift was observed that was ultimately traced to the formation of very small air bubbles on the cell windows. Cleaning the cell in hot concentrated nitric acid was successful in preventing the recurrence of this problem. On another occasion, a very erratic signal was recorded during a blank run. Apparently, small crystals of barium chloranilate penetrated the filter at the bottom of the reaction bed and were pumped into the photometer cell. A glass fiber filter placed in the line between the barium chloranilate cartridge and the cell was effective in preventing further breakthrough of the crystals. Although we encountered only one incidence of pump failure during the laboratory evaluation, we experienced some difficulty in maintaining a constant solution flow rate over an 8-h time interval. Presumably, the fluctuation in flow rate was due to an undetermined inconsistency in the operational characteristics of the pump.

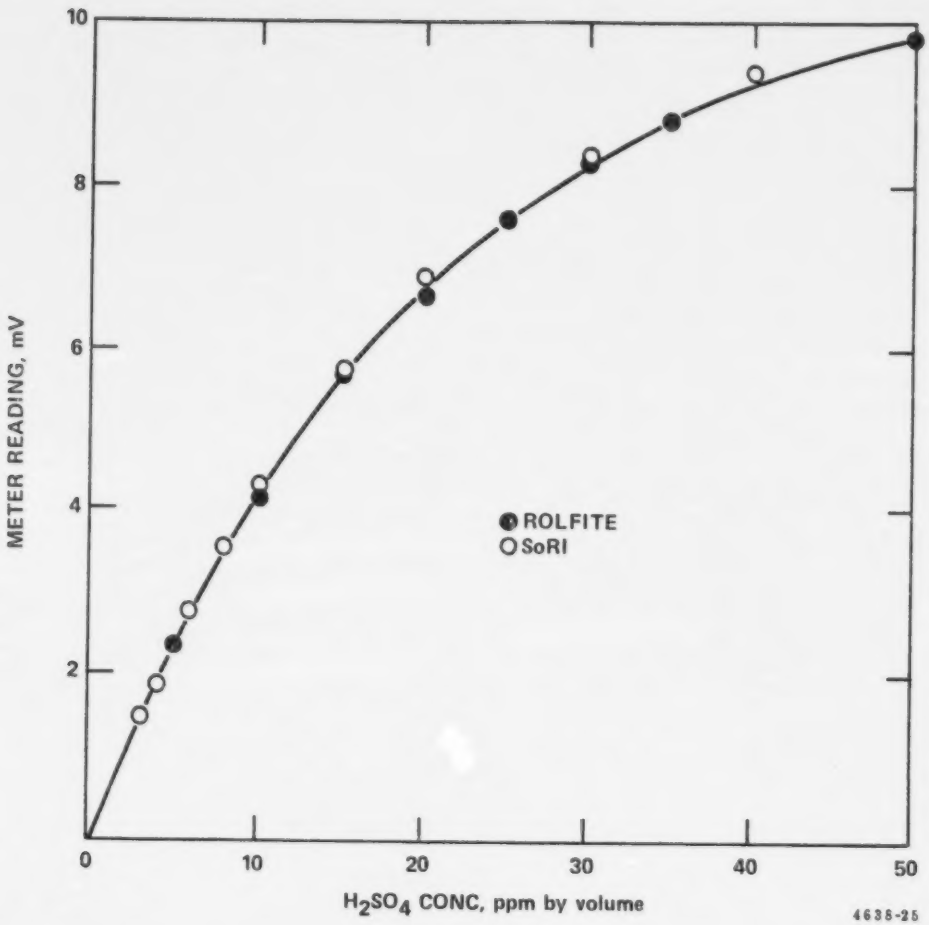

Figure 8. Calibration curve A803 SSL.

SECTION 5

FIELD COMPARISON OF THE AUTOMATED SAMPLING SYSTEM WITH THE MANUAL SYSTEM

SELECTION OF A TEST SITE

At the outset of the project, we conducted a comprehensive review of potential test sites with emphasis on units burning high-sulfur coal, having flue gas desulfurization (FGD) equipment, and having at least a 100-MW generating capacity.* Unfortunately, negotiations to obtain clearance to these stations were unsuccessful. Access to stations burning low-sulfur Western coal was not a problem; however, a low-sulfur coal in conjunction with a highly basic fly ash could yield H_2SO_4 vapor concentrations below 1 ppm in the flue gas. Since the ability of the automated monitors to detect this level of H_2SO_4 reliably was questionable, we obtained approval from the EPA Project Officer to select an alternative site where H_2SO_4 concentrations would be more appropriate for a meaningful comparison of the sampling systems.

Such a site was made available by the Tennessee Valley Authority. Unit No. 10 of the Johnsonville Steam Plant, New Johnsonville, Tennessee, provided accessible sampling facilities at both the inlet and outlet of the ESP. This unit, burning a 2 to 3% sulfur coal in a split-wall, center-fired boiler manufactured by the Foster Wheeler Company, was rated at a 150-MW capacity. Sampling ports located on each side of the split boiler provided access for the determination of boiler O_2 levels. Separate ducts carried the flue gas from the A and B sides of the boiler to the inlet sampling ports preceding the ESP. A total of six horizontal ports were equally spaced across each duct perpendicular to the gas flow. A similar sampling port arrangement was available at the ESP outlet. Therefore, the H_2SO_4 sampling systems could be compared in areas having both high and low concentrations of particulate matter.

SELECTION OF REPRESENTATIVE INLET SAMPLING PORTS

In order to obtain a meaningful comparison of the performance of each sampling system, selection of representative sampling ports was considered to be of major importance in light of the rather severe problems with air leaking in at the breechings immediately upstream of the inlet sample area.

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*The latter two criteria were originally part of the contract for this work.

A preliminary traverse across the A-side duct indicated temperatures between 99 and 116 °C, whereas the corresponding B duct showed temperatures between 138 and 160 °C. Therefore, only the B-side duct was considered to be suitable for sampling. The results of the velocity-temperature traverse of this duct are given in Table 1. Also included in the table are the O_2 concentrations (obtained at depths equivalent to the length of the sample probes) as determined by a Teledyne Analytical Instruments portable O_2 meter. Traverse point No. 4 was approximately equivalent to the depth of the SAMM and manual probes, while point No. 3 represented the depth of the SSL probe. On the basis of the data in Table 1, ports Nos. 1, 2, and 5 were selected as being the most representative of the inlet site.

SAMPLING PROTOCOL

The field evaluation of the H_2SO_4 sampling systems was scheduled for a five-day test program at the ESP inlet, followed by a similar program at the ESP outlet. Each day's sampling consisted of the collection of at least four manual samples and, if possible, 8-h runs with the SAMM and SSL systems. After each manual run, the probe was washed with 100% isopropanol, the washings were filtered through a pre-washed glass fiber filter, and the filtrate was analyzed for H_2SO_4 in the field by a $Ba(ClO_4)_2$ titration. The probe was then washed with distilled, deionized water, the washings were filtered through the same filter used for the isopropanol wash, and the filtrate was analyzed for "total water-soluble sulfate" (TWSS)* by use of an ion chromatograph in our laboratory in Birmingham, AL. The filter holder, with filter, was processed in a similar manner. Therefore, each manual run resulted in two isopropanol and two water samples in addition to the condenser and SO_2 bubbler samples.

A sample from the conductivity cell of the SAMM was collected at least once a day. The condenser and conductivity cell was rinsed with 35 mL of isopropanol, and the rinse was combined with the original sample for on-site analysis. The SAMM probe was washed at the end of each day's sampling by the same procedure described for the manual probe. The ESP, however, was not cleaned unless absolutely necessary, to eliminate the conditioning period required for a clean ESP to reach equilibrium with H_2SO_4. The 47-mm quartz filter, used as a backup to the ESP, was removed daily and extracted, separately, with both isopropanol and water.

A trap, inserted in the SSL sampling system immediately ahead of the barium chloranilate reaction bed, was used to collect a minimum of one sample per day for on-site analysis. The probe and the filter holder, with quartz wool plug, were also extracted daily, with both isopropanol and water.

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*TWSS is a term used by Cheney and Homolya[2,11] to refer to sulfate that can be extracted in water from particulate matter in the probe or on the filter after H_2SO_4 on this particulate matter is selectively extracted in isopropanol. Use of this term is not meant to imply that the H_2SO_4 dissolved in isopropanol would not dissolve in water.

TABLE 1. VELOCITY, TEMPERATURE, AND O_2 PROFILE, B DUCT, ESP INLET[a]

	Port 1		Port 2		Port 3	
	Velocity and temp		Velocity and temp		Velocity and temp	
Point No.	m/s	°C	m/s	°C	m/s	°C
1	17.8	146	18.2	148	21.8	138
2	18.9	148	19.6	148	22.4	142
3	20.4	150	21.3	149	22.0	144
4	21.4	153	21.8	154	19.7	148
% O_2	7.8		7.9		9.1	
% H_2O			8.0			

	Port 4		Port 5		Port 6	
	Velocity and temp		Velocity and temp		Velocity and temp	
Point No.	m/s	°C	m/s	°C	m/s	°C
1	15.5	141	10.8	146	0	155
2	14.1	148	10.3	151	2.8	160
3	20.8	149	16.9	155	8.6	161
4	22.2	151	19.6	158	8.8	160
% O_2	8.4		7.8		7.1	
% H_2O						

[a]CONDITIONS:

ΔP Duct	26 mmHg
Ambient P	751 mmHg
Ambient T	29 °C
Load	130 MW

Throughout each day, plant operating conditions such as load, coal feed rate, steam generation rate, and boiler O_2 level were recorded at 2-h intervals. Coal samples, obtained twice daily, were combined into a single daily composite for later proximate analysis by Commercial Testing and Engineering Company. A sulfur determination, using a Fisher Sulfur Analyzer System, was included in the proximate analysis.

INLET SAMPLING

The SAMM and the manual sampling system were set up in ports Nos. 1 and 2, respectively, and the SSL was set up in port No. 5. Because of the size, weight, and inflexibility of the SAMM, we experienced a great deal of difficulty in positioning that system to mate it with the sampling probe.

Day 1, 5/29/81

Only limited data were obtained with the SSL and manual systems because numerous problems with the SAMM required the attention of the sampling crew. After these problems had been eliminated and the SAMM appeared to be operational, the refrigeration unit on the methanol chiller system failed. A makeshift cooling system consisting of a coil of copper tubing immersed in an ice bath was used as a replacement. Initial tests with this system, however, seemed to indicate that methanol vapor from the rinse cycle was not being completely condensed.

Preliminary results from the abbreviated SSL run indicated an H_2SO_4 concentration of 11 ppm, whereas a value of 10 ppm was obtained on the single manual run.

Day 2, 5/30/81

Further attempts to increase the efficiency of the replacement cooling system in the SAMM were only partially successful; therefore, the methanol rinse cycle was eliminated. Inasmuch as all other components of the SAMM appeared to be operating properly, the instrument was connected to the probe, and sampling was initiated. An apparent overload of the electrical system, however, caused the main circuit breakers to trip, and power was lost to all sampling systems. A separate electrical circuit for SAMM was installed and the instrument was placed back on line for a brief period of sampling. On the basis of an expected 10-ppm concentration of H_2SO_4 in the flue gas, SAMM was operated with a 90% isopropanol/water solution, a 590-s sampling cycle, and a flow rate of 10 L/min. The current in the power supply to the ESP was maintained between 40 and 50 μA. All connections involving the probe, the ESP, and the inlet to SAMM were heat traced and insulated to prevent condensation of H_2SO_4 in these areas. The probe and ESP temperatures were set at 270 °C during sampling.

Prior to sampling, we checked the SSL with several standard solutions of H_2SO_4 to validate the calibration curve and then placed the SSL on line at 1200 hours. This system ran continuously at a sampling rate of 0.5 L/min and a solution flow rate of 2.0 mL/min until 1500 hours, when a power failure occurred. The SSL ran for an additional hour after power had been restored. The probe and filter assembly were held at 200 °C during all sampling.

Four manual samples were collected throughout the day.

A comparison of H_2SO_4 concentrations obtained from the various sampling systems is shown in Figure 9. Considerable variation in apparent H_2SO_4 concentrations was observed with the SSL. Whether these fluctuations were actually representative of changes in acid concentration or were due to undetected instrumental problems could not be determined. A sample collected ahead of the reaction bed indicated an H_2SO_4 concentration of 9 ppm, while the recorder indicated 12 ppm (Appendix A, Table A-7). Plant operating data (Appendix A, Table A-1) showed stable boiler conditions until 1500 hours, when load was reduced from 133 to 125 MW. The proximate analysis of a composited morning and afternoon coal sample (Appendix A, Table A-2) indicated that the sulfur content of the "as received" coal was 2.48%, but obviously short-term changes in the coal supply would not be reflected by this composite analysis.

The distribution of sulfate in the manual and SSL system, as well as the SO_2 concentration obtained from the manual system, are presented in Appendix A, Tables A-4 and A-5, respectively. Because of the very short run time, SAMM probe and filter samples were not obtained. With the exception of run No. 5 with the manual system, where 1.3 ppm of H_2SO_4 was recovered from the isopropanol filter wash, no holdup of H_2SO_4 was observed in either of the sampling systems.

An evaluation of the results indicates that either the H_2SO_4 concentration of the flue gas is subject to rapid and significant changes or the performance of the sampling systems is no better than the scatter shown in Figure 9 indicates.

Day 3, 5/31/81

A calibration check of the SAMM, made with H_2SO_4 standards in a 90% isopropanol/water solution, was in good agreement with the expected response; therefore, sampling was initiated at 1130 hours. After less than 2 h of operation, however, an apparent malfunction in the three-way solenoid between the condenser and the conductivity cell resulted in venting of the sample to the alcohol chiller cabinet instead of to the conductivity cell. After the system had been dismantled, we found a loose connection, rather than the solenoid valve, to be responsible for the problem. The monitor was then placed back in service for a brief period of sampling. We experienced no apparent problems with either of the other sampling systems.

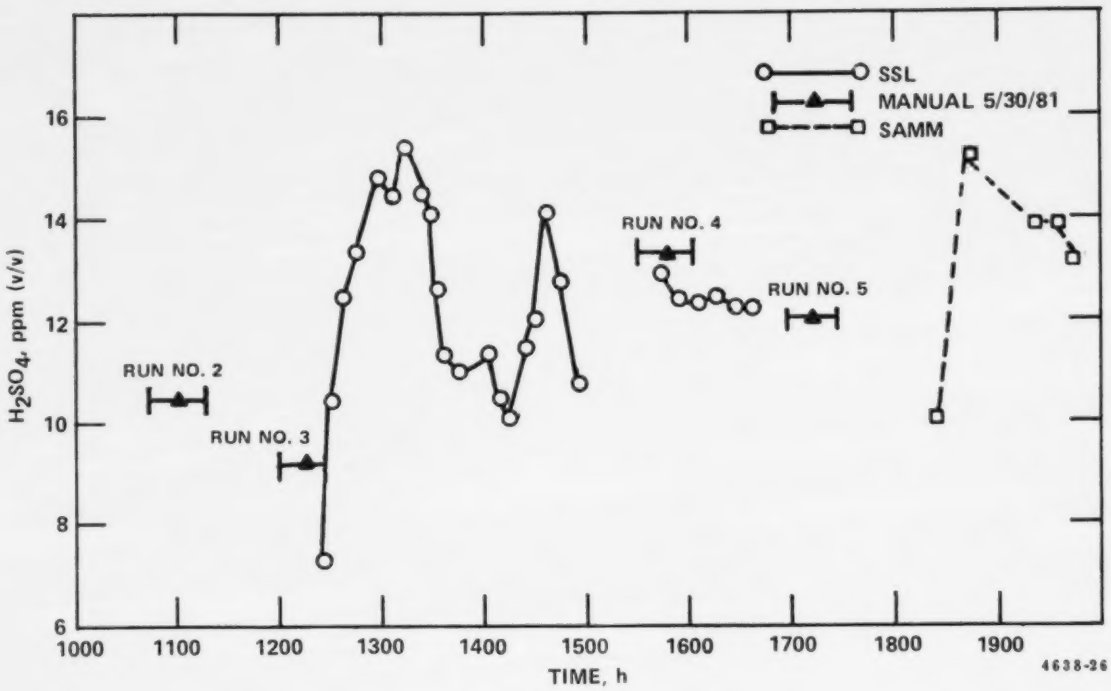

Figure 9. Comparison of H_2SO_4 responses, day 2, inlet.

Figure 10 presents the H_2SO_4 concentrations obtained from the samplers over the day's sampling. After an initial value of 14 ppm of H_2SO_4 and 2110 ppm of SO_2, the manual method gave 7.7 ppm of H_2SO_4 and 1830 ppm of SO_2, representing a very significant decrease in the acid level but only a 13% decrease in the SO_2 concentration. The SSL also indicated a decreased H_2SO_4 level over approximately this same time interval. It may be significant that soot blowing occurred during the entire sampling period for the manual run as well as during that period when the SSL response was at a minimum. Other positive fluctuations were recorded by the SSL over the day's sampling. As before, the validity of these peaks could not be confirmed.

The plant was stable at 125 MW throughout the day. The sulfur content of the coal supply was 2.93%, while the average SO_2 concentration from the manual runs was 1940 ppm. Some condensed H_2SO_4 was found in the manual probe on run No. 8 (2 ppm) and in the SSL probe (1 ppm) run No. 2. No significant holdup was observed in the SAMM or in the filters from the SSL and manual systems.

Day 4, 6/1/81

We encountered several problems with the SAMM during warm-up: (1) the conductivity probe would not remain seated in the conductivity cell during the vent cycle, (2) the vacuum line between the measuring cell and the downstream solenoid valve showed a tendency to collapse, and (3) the solenoid valve between the isopropanol measuring cell and the condenser would open fully only intermittently. After the necessary repairs had been completed, the SAMM went on line at 1200 hours and ran without incident until 1700 hours, when the three-way solenoid valve between the condenser and the conductivity cell began opening only on occasional cycles, resulting in the loss of the sample.

The H_2SO_4 results, as determined by the three systems, are given in Figure 11. The large excursion recorded by the SSL monitor at 1600 hours was not observed by either the SAMM or the manual method. Perhaps this excursion was the result of instrumental problems rather than an actual change in H_2SO_4 levels. Since the SO_2 concentration obtained on this run was only 1570 ppm, as compared to an average of 1960 ppm from the preceding runs, the possibility of a leak in the sampling system cannot be discounted.

The load level of the plant remained at about 130 MW during the period of sampling. The sulfur content of the coal composite was 2.52%, a drop from the 2.93% value obtained the day before. Essentially no H_2SO_4 was detected in the probes of any of the systems, but the equivalent of approximately 1 ppm of H_2SO_4 was extracted from the SSL filter and the filter from the manual samples in runs Nos. 10 and 11.

Day 5, 6/2/81

During the startup of the SAMM, the signal from the mass flow controller was erratic, and we experienced difficulty in setting the flow rate to 10 L/min. The quartz wool plug in the condenser was then changed and the system leak checked. Since no further problems with the flow system were apparent, we

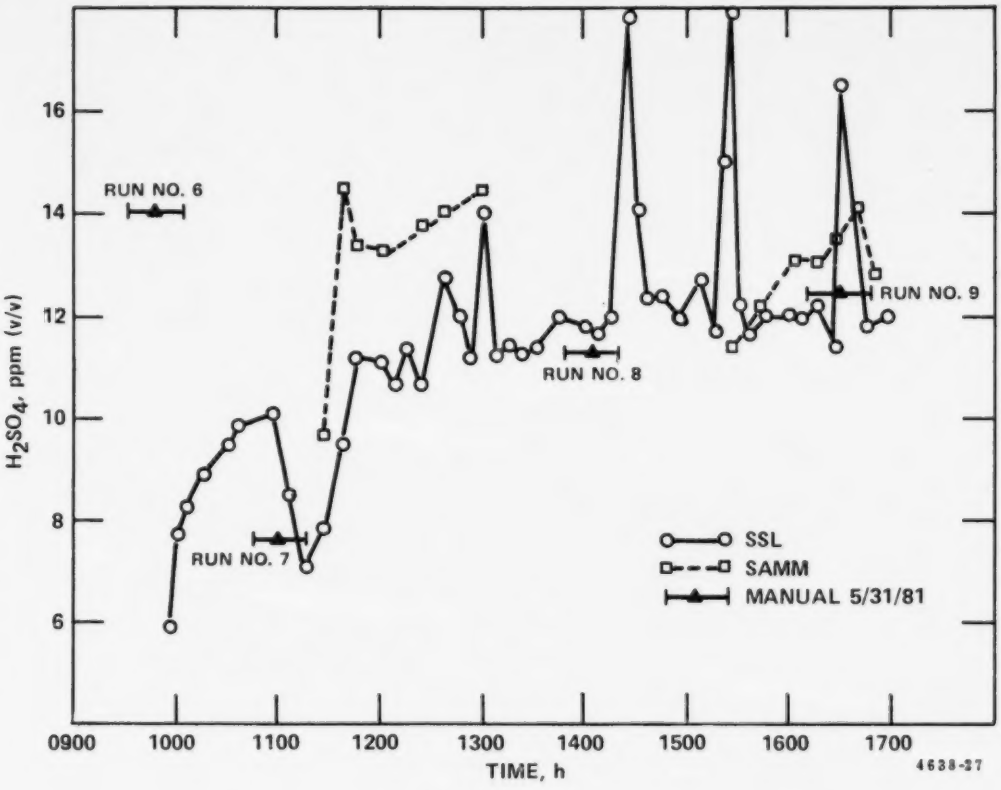

Figure 10. Comparison of H_2SO_4 responses, day 3, inlet.

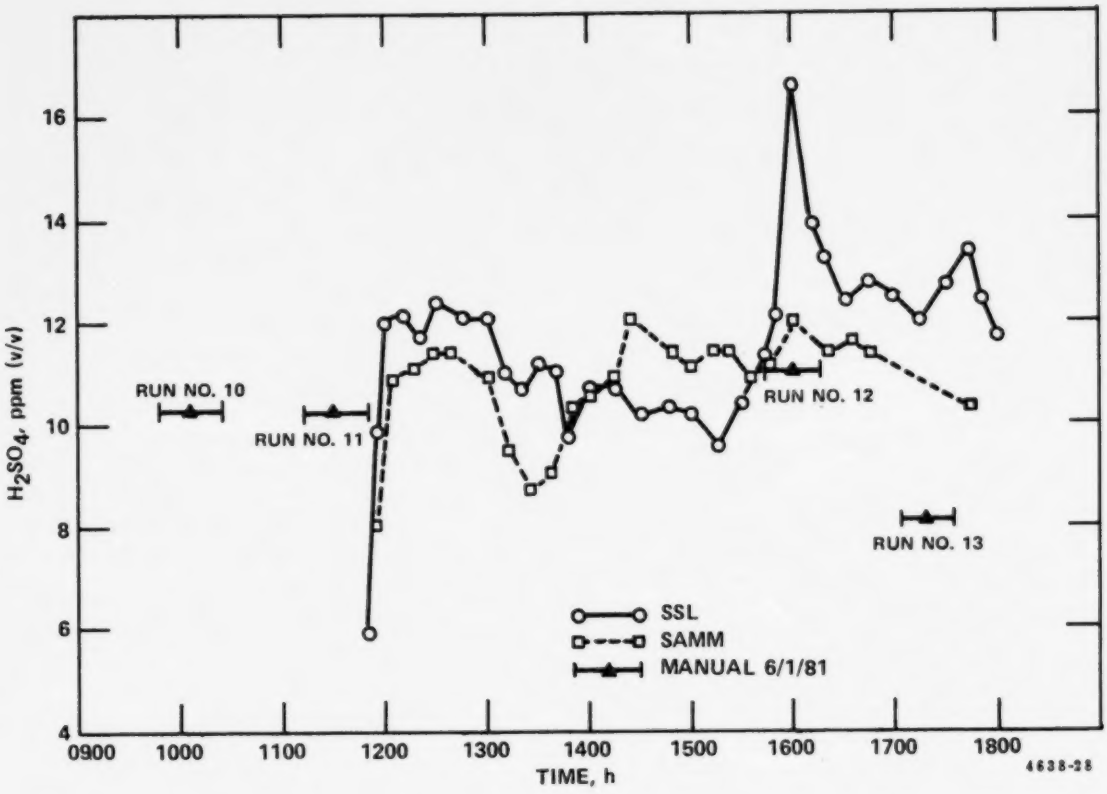

Figure 11. Comparison of H_2SO_4 responses, day 4, inlet.

began sampling with the SAMM at 1130 hours. After 2 h of operation, a leak in the isopropanol system necessitated a shutdown. As shown in Figure 12, the SAMM response after going back on line was appreciably lower than before, although the other systems did not show a corresponding decrease in H_2SO_4 levels. Analysis of a conductivity cell sample from the SAMM indicated an H_2SO_4 concentration of 6.2 ppm, a value that was in good agreement with the conductivity meter. No H_2SO_4 was detected in the isopropanol wash of the probe and filter; therefore, the most plausible explanation for the low results was a possible leak in the system between the condenser and the sample probe.

The SSL response during the 8-h sampling period varied considerably. The apparent peak concentrations of H_2SO_4, moreover, were not reflected in the responses of the other systems. All four manual runs indicated the H_2SO_4 concentration to be about 9 ppm and the SO_2 concentration to be about 1900 ppm. No appreciable holdup of acid occurred in the probe or filter of any of the systems.

The plant was operated at 135 MW until 1430 hours and at 141 MW for the remainder of the test period. Soot blowing occurred between 1030 and 1130 hours and again between 1700 and 1800 hours.

OUTLET SAMPLING

A velocity-temperature transverse and an O_2 profile across the B duct at the outlet of the ESP was obtained prior to the selection of representative sampling ports. On the basis of the data obtained, shown in Table 2, ports Nos. 2, 3, and 5 were assigned to the SSL, manual, and SAMM sampling systems, respectively. Two manual runs showed H_2SO_4 concentrations to be about 4 ppm and SO_2 levels to be about 1800 ppm.

Day 6, 6/4/81

The mass flow controller on the SAMM was extremely erratic, therefore, a dry gas meter, protected by silica gel towers, was used to monitor gas sampling rates. The actual sampling cycle on the SAMM was also increased to 665 s, since lower H_2SO_4 levels were expected at the ESP outlet. The SAMM finally began sampling at 1300 hours and ran until the termination of the test at 1830 hours.

The SSL operated without problems until 1530 hours, when the head on the extraction pump began binding, necessitating a shutdown of the instrument. The ceramic piston-and-cylinder assembly was dismantled and cleaned with isopropanol to restore it to working condition.

All three systems showed moderately good agreement in H_2SO_4 concentrations measured. The results, given in Figure 13, indicate the H_2SO_4 concentration to be about 4 ppm, a significantly lower level than that observed at the ESP inlet. The decrease might be expected as a result of the increased contact time of the H_2SO_4 vapor with the fly ash particles across the ESP.

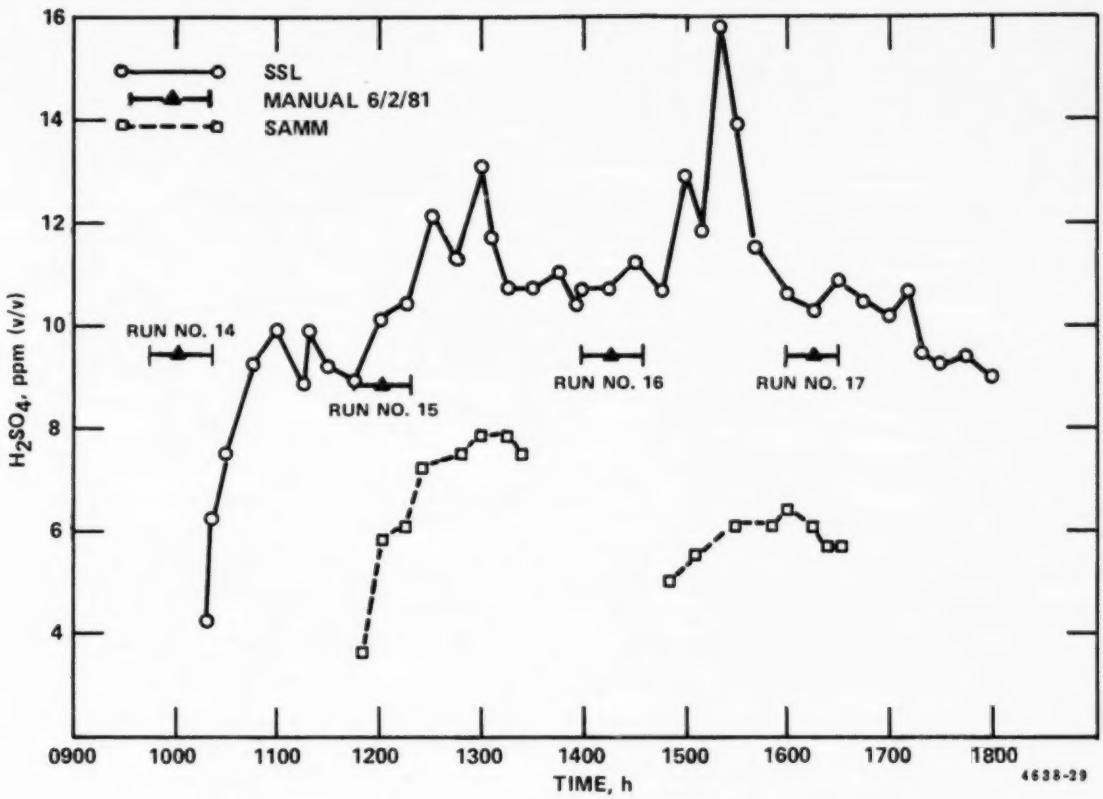

Figure 12. Comparison of H_2SO_4 responses, day 5, inlet.

TABLE 2. VELOCITY, TEMPERATURE, AND O_2 PROFILE, B DUCT, ESP OUTLET[a]

	Port 1		Port 2		Port 3	
	Velocity and temp		Velocity and temp		Velocity and temp	
Point No.	m/s	°C	m/s	°C	m/s	°C
1	12.6	144	13.4	144	13.4	143
2	12.4	144	10.9	145	10.9	144
3	12.2	144	8.2	146	8.0	144
4	12.2	143	8.2	145	7.0	143
% O_2	7.7		7.4		7.5	
% H_2O					7.9	

	Port 4		Port 5		Port 6	
	Velocity and temp		Velocity and temp		Velocity and temp	
Point No.	m/s	°C	m/s	°C	m/s	°C
1	12.5	142	12.7	143	13.6	141
2	10.8	144	10.1	144	12.5	141
3	8.0	144	8.2	144	9.6	142
4	7.2	143	7.2	144	6.7	143
% O_2	7.7		7.4		7.3	
% H_2O						

[a]CONDITIONS:

ΔP Duct	34 mmHg
Ambient P	751 mmHg
Ambient T	26 °C
Load	132 MW

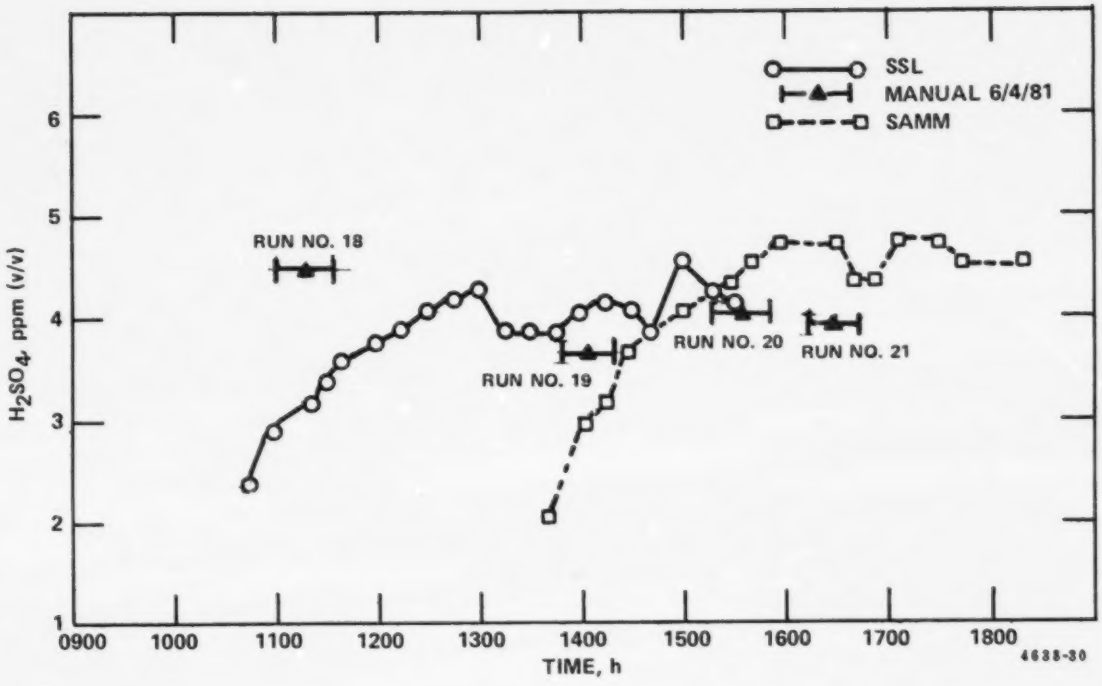

Figure 13. Comparison of H_2SO_4 responses, day 6, outlet.

No holdup of H_2SO_4 was detected in the probe and filter of the SSL and manual system or in the SAMM probe. The SAMM filter could not be recovered because the filter holder resisted all attempts to disassemble it.

The plant maintained a constant load of 140 MW during testing. A proximate analysis of the coal composite showed the sulfur content to be 2.55%. The average SO_2 concentration obtained from the manual runs was 1780 ppm.

Day 7, 6/5/81

All systems operated without incident during an 8-h sampling period with the plant at 141 to 145 MW. Although no problems were apparent, the data in Figure 14 show significant differences among the H_2SO_4 concentrations determined by the various systems, especially between 1500 and 1730 hours. During this time, the SSL indicated increased acid levels, whereas the SAMM and manual samplers both indicated decreases in the H_2SO_4 concentration. Since no appreciable levels of H_2SO_4 were found in either the probe or the filters of any of the systems, the reason for this discrepancy was not apparent. SO_2 values decreased from 1875 to 1625 ppm during the day, with an abnormally low value of 1475 ppm found on run No. 26. The daily coal composite analysis indicated the sulfur content of the coal to be 2.32%.

Day 8, 6/7/81

With the exception of the time between 1130 and 1230 hours when the SAMM and manual systems showed a decrease in H_2SO_4 and the SSL did not, reasonably good agreement was obtained among the samplers (Figure 15). As before, there was no apparent reason for this discrepancy. Plant conditions were stable at 124 MW throughout the day, and no significant loss of H_2SO_4 in the probe or filters was observed. The sulfur content of the coal was 2.45%, and the average SO_2 concentration in the flue gas was 1600 ppm. SO_2 levels appeared to increase, however, from 1515 ppm at 1430 h to 1720 ppm at 1730 h.

Day 9, 6/8/81

All three sampling systems were relatively consistent during this day's run, with the exception of a large excursion by the SSL between 1630 and 1700 hours. This excursion appeared to be an artifact because such an increase in H_2SO_4 was not reflected in the other two systems. A further examination of the data shown in Figure 16 indicated a low recovery of H_2SO_4 by the manual system, although a rigorous examination of this unit failed to disclose any problems. The possibility of poor efficiency in the collection of H_2SO_4 by the glass plug condensers was also explored by connecting two condensers in series on two separate runs. The results of these tests showed recoveries of 86 and 94% of the acid in the lead condenser.

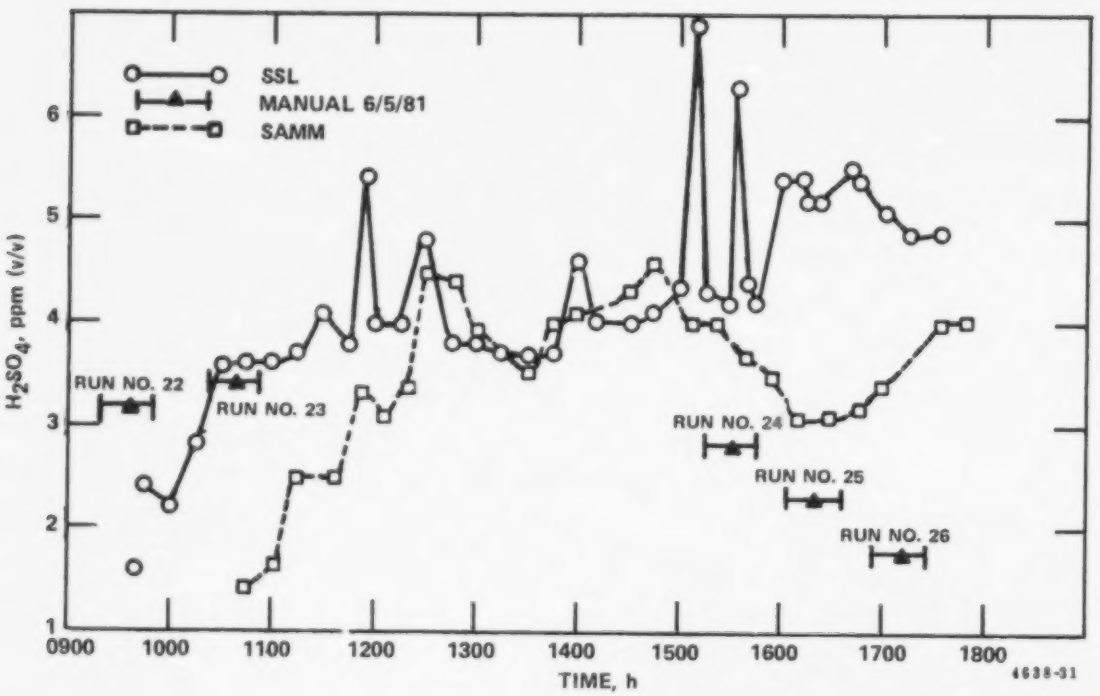

Figure 14. Comparison of H_2SO_4 responses, day 7, outlet.

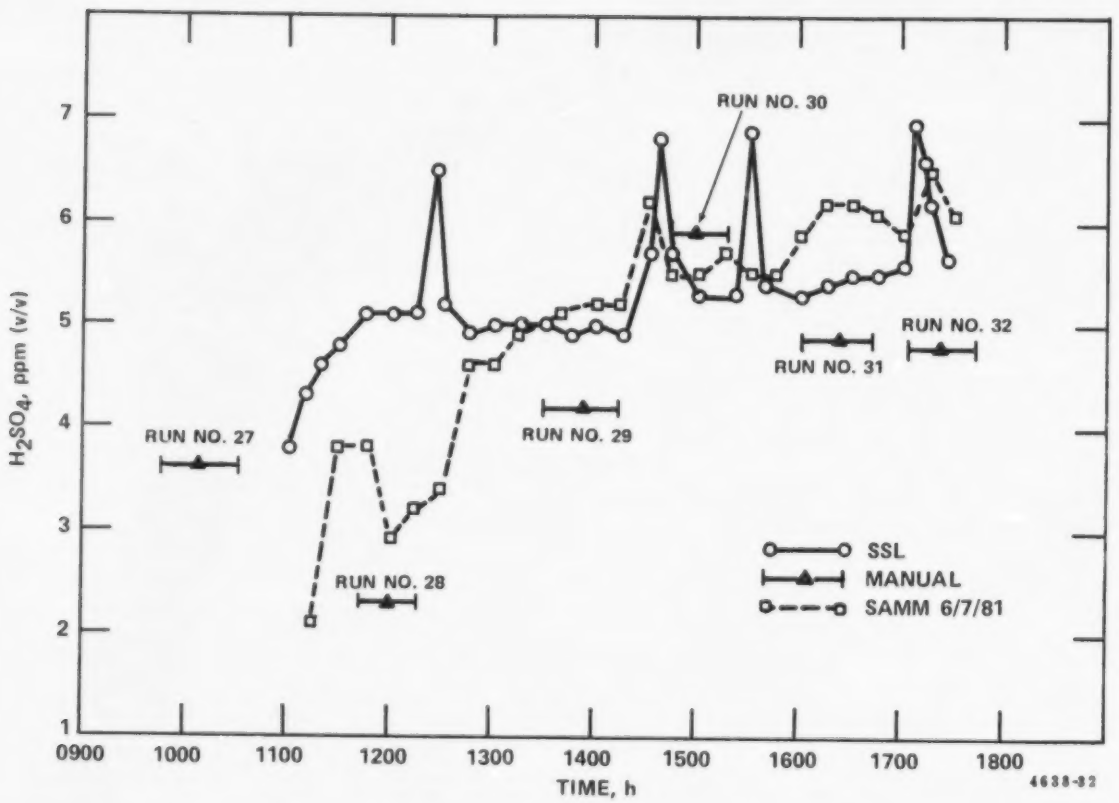

Figure 15. Comparison of H_2SO_4 response, day 8, outlet.

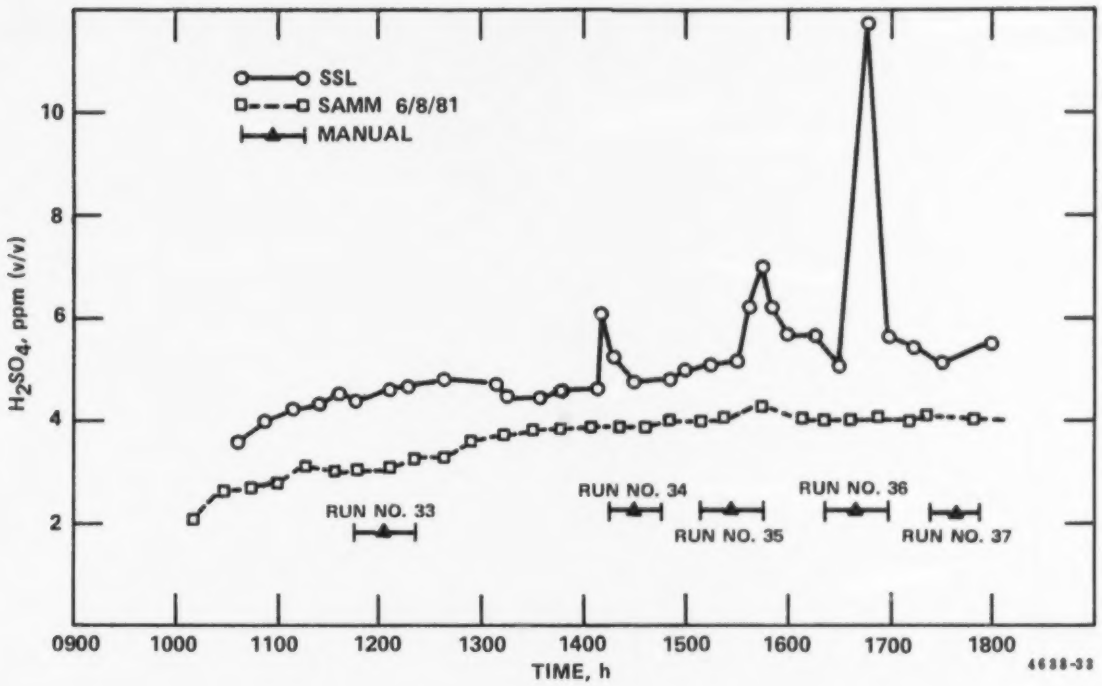

Figure 16. Comparison of H_2SO_4 responses, day 9, outlet.

The SO_2 values were consistent throughout the day, with an average concentration of 2040 ppm, reflecting the higher sulfur content of the coal supply, 2.90%. The plant maintained a 137-MW load over the course of the day's testing.

Day 10, 6/9/81

The plant, burning coal with a sulfur content of 2.44%, was held at 130 MW throughout the final day of the test program. Both automated monitors were operated without problems and, as shown in Figure 17, were in generally good agreement with each other. On the other hand, several of the manual runs indicated H_2SO_4 concentrations to be 1 to 2 ppm lower than those measured by the other systems. Somewhat higher than expected H_2SO_4 holdup was observed in the probe (0.6 ppm) and filter holder (0.4 ppm) of the manual system, although temperatures were maintained at the usual 270 °C. SO_2 values averaged 1750 ppm for the initial three runs, but dropped to 1620 and 1535 ppm on the final two runs. Since the system was checked for leaks and found to be satisfactory following the final run, the difference between the manual and automated systems was not resolved.

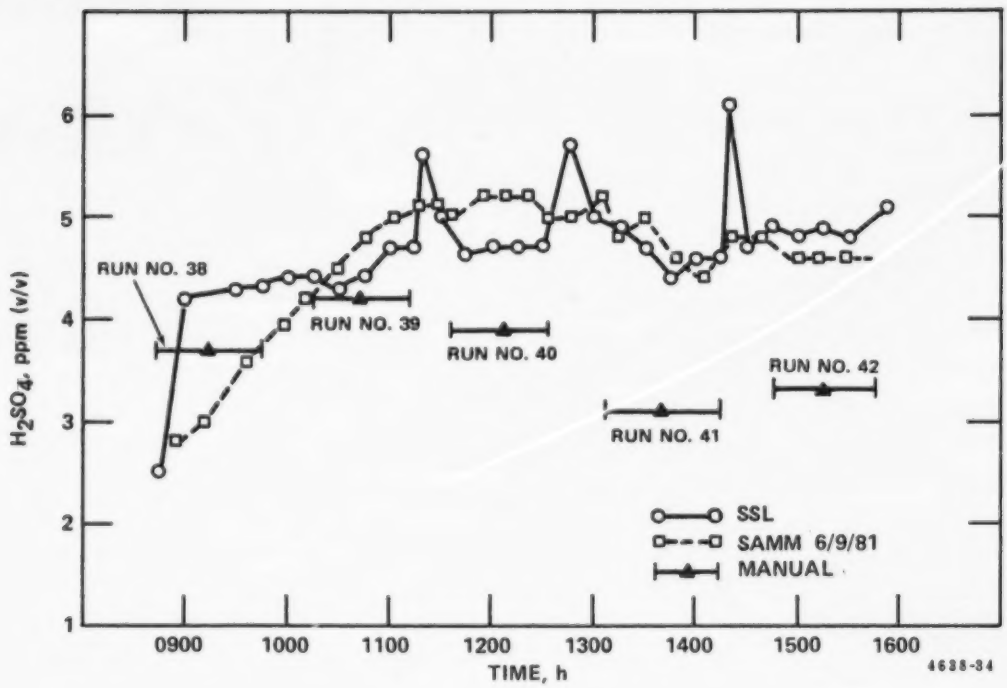

Figure 17. Comparison of H_2SO_4 responses, day 10, outlet.

SUMMARY

The average daily H_2SO_4 concentration obtained from the three sampling systems at the inlet and outlet of the ESP is shown in Figures 18 and 19, respectively. These data for each sampler were compiled by averaging the results from the integrated SSL response, each SAMM cycle, and each manual run.

The H_2SO_4 concentration at the inlet appeared to be in the range of 10 to 13 ppm, a level not inconsistent with the sulfur content of the coal and the dilution effect resulting from air leaking in upstream of the sampling ports. The SSL, in general, showed the highest H_2SO_4 concentrations; the manual method the lowest. Assuming the day 5 SAMM response to be an outlier, the spread among the systems was no greater than 2 ppm (or about 20% relative) on any particular day.

A significant decrease of approximately 8 ppm in the H_2SO_4 level to a level of about 4 ppm was indicated by all systems at the ESP outlet, presumably due to uptake of the acid by the fly ash across the ESP. Agreement among the three systems was within 1 ppm (or about 25% relative) for each individual day except for the day 9 results. The reason for the wider spread in the data on that day is unknown.

Submitted by:

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Analytical and Physical
Chemistry Division

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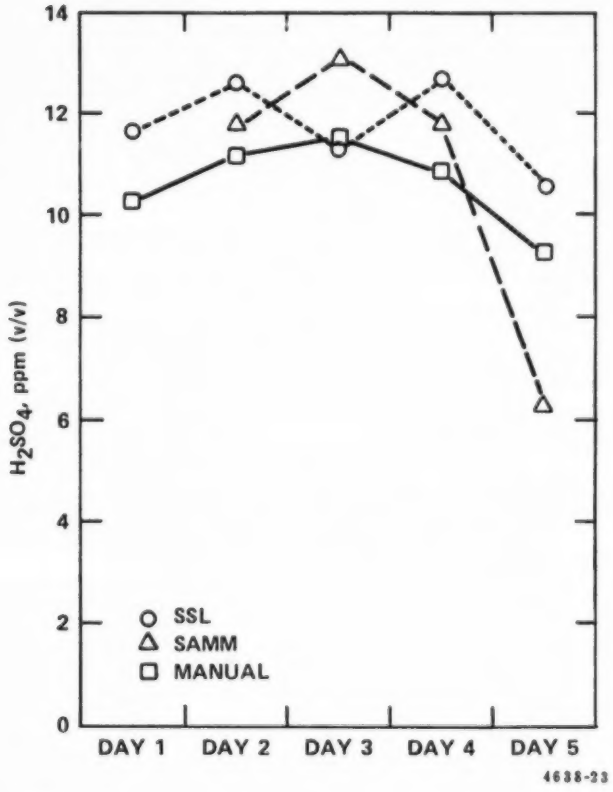

Figure 18. Comparison of average inlet H_2SO_4 concentrations found by three methods.

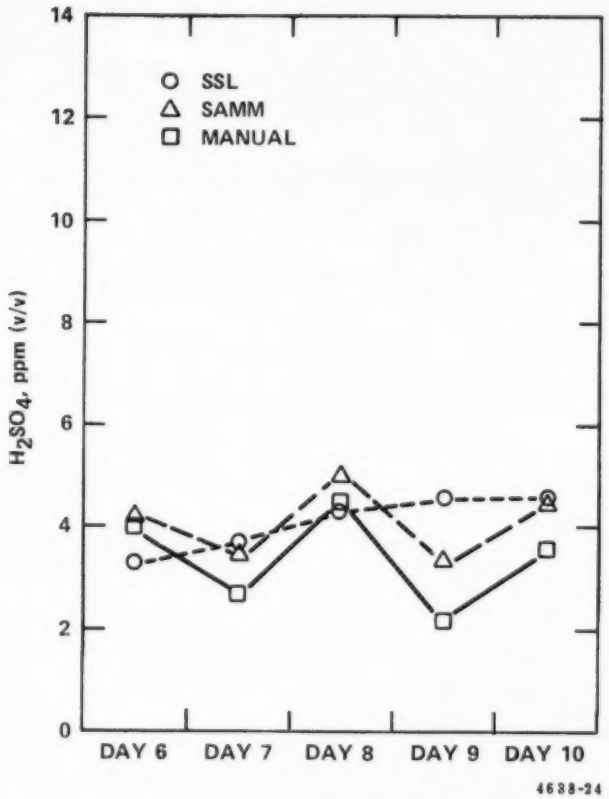

Figure 19. Comparison of average outlet H_2SO_4 concentrations found by three methods.

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APPENDIX A

SUPPLEMENTARY DATA RELATIVE TO THE FIELD EVALUATION OF SULFURIC ACID SAMPLING SYSTEMS

This appendix contains ancillary data, obtained either during the field evaluation of the H_2SO_4 sampling systems or in the laboratory subsequent to the field test.

Plant operating conditions (Table A-1)
Proximate coal analyses (Table A-2)
Mineral analysis of coal ash (Table A-3)
Distribution of sulfate:

- Manual sampling system (Table A-4)
- SSL sampling system (Table A-5)
- SAMM sampling system (Table A-6)

Sulfuric acid concentrations:

- SSL samples collected ahead of the reaction bed (Table A-7)
- SAMM conductivity cell samples (Table A-8)

TABLE A-1. PLANT OPERATING CONDITIONS: UNIT NO. 10

Date	Time	Load, MW	Steam flow, lb/h x 1000	Air flow rate, ACFM x 1000	Boiler O_2, %	Coal feed rate, ton/h
5/30/81	0900	133	835	960		
	1100	132	835	960	3.8	56
	1300	133	835	960		53
	1500	125	775	875		55
	1700	123	775	875	4.2	53
5/31/81	0900	125	800	900		
	1100	125	800	900		53
	1300	125	800	900	4.0	61
	1500	125	800	900		62
	1700	126	800	900		54
6/1/81	0900	130	825	900		
	1100	130	825	900		56
	1300	133	825	900	3.9	56
	1500	132	825	910		62
	1700	132	825	910		55
6/2/81	0900	135	850	915		
	1100	134	850	915		
	1300	135	850	915		
	1500	141	900	965	2.8	—[a]
	1700	141	910	975		
6/4/81	0900	140	900	950		
	1100	140	900	950		
	1300	140	900	950	3.4	—[a]
	1500	140	900	950		
	1700	140	900	950		
6/5/81	1000	141	900	950		
	1100	142	900	950		
	1300	142	900	950		—[a]
	1500	143	900	950	3.2	
	1700	145	920	935		
6/7/81	1000	125	785	850		
	1100	124	785	850		51
	1300	124	780	835		58
	1500	124	780	835	4.3	52
	1700	123	780	835		59

(continued)

TABLE A-1 (continued)

Date	Time	Load, MW	Steam flow, lb/h x 1000	Air flow rate, ACFM x 1000	Boiler O_2, %	Coal feed rate, ton/h
6/8/81	0900	136	875	950		
	1100	137	875	950		60
	1300	137	875	950	3.4	66
	1500	137	875	950		69
	1700	135	850	900		65
6/9/81	0800	130	825	900		
	1000	130	825	900		56
	1200	130	825	900		58
	1400	131	800	875	3.8	67
	1600	130	800	875		66

[a]Mill problems.

TABLE A-2. PROXIMATE COAL ANALYSES[a]

Date	Moisture, %	Ash, %	Volatile, %	Fixed carbon, %	Sulfur, %	BTU/lb
5/30/81	14.27	11.15	32.74	41.84	2.48	10856
5/31/81	15.27	13.94	31.23	39.56	2.93	10265
6/1/81	14.09	11.22	32.99	41.70	2.52	10874
6/2/81	11.97	11.89	33.50	42.64	2.25	10938
6/4/81	12.78	14.15	30.60	42.47	2.55	10918
6/5/81	10.94	10.89	33.67	44.50	2.32	11207
6/7/81	12.38	11.95	33.07	42.60	2.45	11058
6/8/81	13.61	14.20	31.99	40.20	2.90	10400
6/9/81	14.50	11.72	33.18	40.60	2.44	10731

[a]Daily coal samples were prepared by compositing equal weights of coal obtained from morning and afternoon grab samples.

TABLE A-3. MINERAL ANALYSIS OF COMPOSITED COAL ASH[a]

Element, as oxide	Concentration, wt %
Al_2O_3	22.5
CaO	2.3
Fe_2O_3	18.8
K_2O	2.3
Li_2O	0.03
MgO	0.89
Na_2O	0.32
P_2O_5	0.48
SiO_2	48.8
SO_3	2.5
TiO_2	1.3

[a]Ten-day coal composite, ashed at 750 °C.

TABLE A-4. CONCENTRATIONS OF SULFUR DIOXIDE, SULFURIC ACID AND SULFATE DETERMINED WITH THE MANUAL SAMPLING SYSTEM

Date	Location	Run No.	Time	Total sample volume, L	SO_2, ppm	H_2SO_4 or SO_4^{-2} expressed as H_2SO_4, ppm[a]					Total H_2SO_4,[b] ppm	Total water-soluble sulfate (TWSS),[c] ppm	$\frac{H_2SO_4 \times 100}{H_2SO_4 + TWSS}$
						In probe		On filter					
						Isopropanol-soluble	Water-soluble	Isopropanol-soluble	Water-soluble	In condenser			
5/29/81	Inlet	1	1443-1520	38.5	1810	0.06	3.2	0.75	2.7	9.5	10.3	5.9	64
5/30/81	Inlet	2	1040-1120	52.0	1825	0.05	0.58	0.12	2.9	10.1	10.3	3.5	75
	Inlet	3	1200-1230	37.9	1575	0.03	0.34	0.10	2.8	9.1	9.2	3.1	75
	Inlet	4	1530-1607	38.4	2010	0.10	0.69	0.26	2.1	12.8	13.2	2.8	82
	Inlet	5	1658-1725	36.1	1830	0.03	0.38	1.3	2.0	10.7	12.0	2.4	83
5/31/81	Inlet	6	0934-1003	38.6	2110	0.03	0.52	0.06	2.0	14.0	14.1	2.5	85
	Inlet	7	1042-1114	37.1	1830	0.07	0.37	0.78	3.7	6.9	7.7	4.1	65
	Inlet	8	1350-1420	35.1	1870	2.0	0.97	0.21	2.0	9.1	11.3	3.0	79
	Inlet	9	1610-1648	38.0	1935	0.13	0.70	0.40	1.3	12.1	12.6	2.0	86
6/1/81	Inlet	10	0950-1027	38.5	2060	<0.02	0.54	1.1	2.8	9.2	10.3	3.3	62
	Inlet	11	1112-1150	38.0	1940	<0.02	0.57	1.2	2.0	9.0	10.2	2.6	80
	Inlet	12	1540-1615	38.0	1890	<0.02	0.36	0.17	1.6	10.8	11.0	2.0	85
	Inlet	13	1703-1735	38.1	1570	<0.02	0.23	0.16	1.2	7.9	8.1	1.4	85
6/2/81	Inlet	14	0944-1020	38.8	2055	<0.02	0.58	0.10	2.0	9.3	9.4	2.6	78
	Inlet	15	1145-1218	38.0	1875	0.03	0.32	0.03	1.9	8.7	8.8	2.2	80
	Inlet	16	1400-1435	38.0	1815	0.20	1.0	0.13	1.8	9.2	9.5	2.8	77
	Inlet	17	1602-1632	38.5	1850	<0.02	0.38	0.10	1.2	9.3	9.4	1.6	85
6/4/81	Outlet	18	1056-1148	59.4	2090	<0.02	0.26	<0.02	0.38	4.4	4.4	0.64	87
	Outlet	19	1345-1420	40.8	1650	<0.02	0.43	0.15	0.63	3.6	3.8	1.1	78
	Outlet	20	1518-1555	41.7	1715	<0.02	0.38	0.09	0.38	3.9	4.0	0.76	84
	Outlet	21	1613-1646	38.0	1665	<0.02	0.61	0.06	0.12	3.8	3.9	0.73	84
6/5/81	Outlet	22	0922-0956	40.8	1875	<0.02	0.52	<0.02	0.37	3.2	3.2	0.89	78
	Outlet	23	1020-1054	38.1	1970	<0.02	0.38	<0.02	0.38	3.5	3.5	0.76	82
	Outlet	24	1515-1547	32.8	1475	<0.02	0.37	0.08	0.44	2.7	2.8	0.81	78
	Outlet	25	1603-1634	34.8	1715	<0.02	0.22	0.18	0.35	2.1	2.3	0.57	80
	Outlet	26	1655-1725	35.7	1625	<0.02	0.24	0.24	0.39	1.6	1.8	0.63	75

(Continued)

TABLE A-4 (continued)

Date	Location	Run No.	Time	Total sample volume, L	SO_2 ppm	H_2SO_4 or SO_4^{-2} expressed as H_2SO_4, ppm[a]							
						In probe		On filter					
						Isopropanol-soluble	Water-soluble	Isopropanol-soluble	Water-soluble	In condenser	Total H_2SO_4, ppm[b]	Total water-soluble sulfate (TWSS),[c] ppm	$\frac{H_2SO_4 \times 100}{H_2SO_4 + TWSS}$
6/7/81	Outlet	27	0952-1024	38.1	1545	0.03	0.35	0.10	0.49	3.5	3.6	0.84	81
	Outlet	28	1138-1213	38.1	1515	0.10	0.70	0.10	0.38	2.1	2.3	1.1	68
	Outlet	29	1348-1420	37.9	1515	0.10	0.21	0.33	0.44	4.2	4.6	0.65	88
	Outlet	30	1447-1521	38.1	1595	0.10	0.67	<0.02	0.42	5.8	5.9	1.1	84
	Outlet	31	1604-1642	37.7	1690	0.23	0.40	0.10	0.45	4.9	5.2	0.95	85
	Outlet	32	1703-1736	37.6	1720	0.22	0.47	0.07	0.52	4.8	5.1	0.99	84
6/8/81	Outlet	33	1140-1220	38.2	2060	<0.02	0.44	<0.02	0.52	1.8	1.8	0.96	65
	Outlet	34	1415-1448	38.0	2020	0.26	0.23	0.26	0.65	1.8	2.3	0.88	72
	Outlet	35	1508-1545	38.0	1940	0.17	0.44	0.26	0.44	1.9	2.3	0.88	72
	Outlet	36	1623-1700	42.0	2050	0.33	0.20	0.24	0.50	1.7	2.3	0.70	77
	Outlet	37	1723-1755	38.0	2130	0.10	0.43	0.07	0.48	2.1	2.3	0.91	72
6/9/81	Outlet	38	0840-0945	62.2	1735	0.48	0.39	0.30	0.36	2.9	3.7	0.75	83
	Outlet	39	1015-1112	50.5	1795	0.70	0.60	0.32	0.33	3.2	4.2	0.93	82
	Outlet	40	1137-1232	50.5	1725	0.70	0.49	0.72	0.52	2.5	3.9	1.0	80
	Outlet	41	1308-1415	58.7	1620	0.53	0.26	0.45	0.61	2.1	3.1	0.87	78
	Outlet	42	1447-1545	50.0	1535	0.45	0.40	0.28	0.43	2.6	3.3	0.83	80

[a]Concentration expressed in parts per million by volume, dry basis.

[b]Total H_2SO_4 expressed as the sum of the condenser, isopropanol, and isopropanol filter extractions.

[c]TWSS expressed as the sum of the water extractions of the probe and filter.

TABLE A-5. DISTRIBUTION OF SULFATE IN THE SSL MONITOR

Date	Location	Total sample volume, L	Concentration, ppm (v/v)				Average SSL response
			Probe		Filter		
			Isopropanol	Water	Isopropanol	Water	
5/29/81	Inlet	75	0.02	0.40	0.38	4.6	≈12
5/30/81	Inlet	148	0.03	0.55	0.23	1.3	≈12
5/31/81	Inlet	200	0.02	1.4	1.0	1.6	≈11
6/1/81	Inlet	180	0.05	0.48	1.2	2.3	≈12
6/2/81	Inlet	212	<0.01	0.15	0.48	2.0	≈11
6/4/81	Outlet	135	<0.01	0.22	0.14	0.50	≈4
6/5/81	Outlet	210	<0.01	<0.01	0.15	0.25	≈4
6/7/81	Outlet	175	<0.01	0.21	0.27	0.24	≈4
6/8/81	Outlet	208	<0.01	0.17	0.18	0.25	≈5
6/9/81	Outlet	210	<0.01	0.14	0.09	0.15	≈5

TABLE A-6. DISTRIBUTION OF SULFATE IN THE SAMM

Date	Location	Total sample volume, L	Concentration, ppm (v/v)				Average SSL response
			Probe		Filter		
			Isopropanol	Water	Isopropanol	Water	
5/30/81	Inlet	745	<0.01	0.15	<0.01	0.06	≃12
5/31/81	Inlet	2729	<0.01	0.10	<0.01	0.04	≃13
6/1/81	Inlet	2103	<0.01	0.17	<0.01	<0.01	≃12
6/2/81	Inlet	2898	<0.01	0.04	—[a]	—[a]	≃6
6/4/81	Outlet	4023	0.01	0.05	<0.01	<0.01	≃4
6/5/81	Outlet	4077	<0.01	0.04	<0.01	<0.01	≃4
6/7/81	Outlet	3752	<0.01	0.05	<0.01	<0.01	≃5
6/8/81	Outlet	4928	<0.01	0.04	<0.01	<0.01	≃3
6/9/81	Outlet	3900	<0.01	0.06	<0.01	<0.01	≃4

[a]Filter could not be recovered from the filter holder.

TABLE A-7. SULFURIC ACID CONCENTRATIONS IN SSL SAMPLES COLLECTED AHEAD OF THE REACTION BED

Date	Location	H_2SO_4, ppm (v/v)	
		Sample[a]	Meter[b]
5/30/81	Inlet	9	12
5/31/81	Inlet	14	12
6/1/81	Inlet	14	12
6/2/81	Inlet	10	9
6/4/81	Outlet	c	c
6/5/81	Outlet	6	5
6/7/81	Outlet	5	6
6/8/81	Outlet	7	6
6/9/81	Outlet	8	6

[a]Sample collected ahead of reaction bed.

[b]Concentration from calibration curve.

[c]Instrument down for repairs before sample collected.

TABLE A-8. SULFURIC ACID CONCENTRATIONS IN SAMM CONDUCTIVITY CELL SAMPLES

Date	Location	H_2SO_4, mg	
		Sample[a]	Meter[b]
5/31/81	Inlet	4.2	4.5
6/1/81	Inlet	3.4	3.4
6/2/81	Inlet	3.0	2.7
6/4/81	Outlet	2.7	2.3
6/5/81	Outlet	2.4	2.4
6/7/81	Outlet	3.9	3.8
6/8/81	Outlet	2.1	2.2
6/9/81	Outlet	3.1	2.9

[a]Milligrams of H_2SO_4 in samples.

[b]Milligrams of H_2SO_4 from meter reading on calibration curve.

APPENDIX B

METHODS USED IN THE CALCULATION OF SULFURIC ACID, SULFUR DIOXIDE, AND SULFATE CONCENTRATIONS

This appendix lists the methods used to calculate the concentration of sulfur species from the raw data obtained by the SSL, SAMM, and manual sampling systems. The pages on which the methods may be found are given below:

	Page
Sulfuric acid concentrations:	
From SAMM chart recordings	54
From SSL chart recordings	54
In SAMM conductivity cell samples	54
In SSL samples collected ahead of the reaction bed and in SAMM, SSL, and manual isopropanol washes of probes and filters	55
Sulfate concentrations:	
In SAMM, SSL, and manual water washes of probes and filters	56
Sulfur dioxide concentrations:	
From manual impinger samples	57

SULFURIC ACID CONCENTRATIONS

From SAMM Chart Recordings

The weight of H_2SO_4, in milligrams, collected during a cycle is obtained from a comparison of the average recorder output against the SAMM calibration curve. The H_2SO_4 concentration is then calculated from the following equation:

$$C_{H_2SO_4} = \frac{(\frac{W_s}{W_m})\ K}{V_m} \qquad (1)$$

where

$C_{H_2SO_4}$ = concentration of H_2SO_4, ppm by volume

W_s = weight of H_2SO_4, mg

W_m = milliequivalent weight of H_2SO_4, 49 mg/meq

K = milliequivalent volume, 11.2×10^3 µL

V_m = volume of gas sampled during a cycle, L

From SSL Chart Recordings

The H_2SO_4 concentration, in parts-per-million by volume, is obtained from a direct comparison of the recorder output against the SSL calibration curve.

In SAMM Conductivity Cell Samples

The weight of H_2SO_4 in conductivity cell samples is obtained from the following equation:

$$W_{H_2SO_4} = (V_t - V_b)N(\frac{V_s}{V_a})W_m \qquad (2)$$

where

$W_{H_2SO_4}$ = weight of H_2SO_4, mg

V_t = volume of $Ba(ClO_4)_2$ used for the sample, mL

V_b = volume of $Ba(ClO_4)_2$ used for the blank, mL

N = normality of $Ba(ClO_4)_2$, meq/mL

V_s = volume of sample, mL

V_a = volume of aliquot titrated, mL

W_m = milliequivalent weight of H_2SO_4, 49 mg/meq

In SSL Samples Collected Ahead of the Reaction Bed and in SAMM, SSL, and Manual Isopropanol Washes of Probes and Filters

The concentration of H_2SO_4 in these samples is calculated as follows:

$$C_{H_2SO_4} = \frac{(V_t - V_b)N(\frac{V_s}{V_a})K}{V_m} \quad (3)$$

where

$C_{H_2SO_4}$ = concentration of H_2SO_4, ppm by volume

V_t = volume of $Ba(ClO_4)_2$ used for the sample, mL

V_b = volume of $Ba(ClO_4)_2$ used for the blank, mL

N = normality of $Ba(ClO_4)_2$, meq/mL

V_s = volume of sample, mL

V_a = volume of aliquot titrated, mL

K = milliequivalent volume, 11.2×10^3 µL

V_m = volume of gas sampled, L

SULFATE CONCENTRATIONS

In SAMM, SSL, and Manual Water Washes of Probes and Filters (Ion Chromatographic Analysis)

The concentration of sulfate in these samples is obtained from the following equation:

$$C_{SO_4} = \frac{(C_s - C_b)V_s K}{\frac{W_m}{V_m}} \qquad (4)$$

where

C_{SO_4} = concentration of sulfate, ppm by volume

C_s = concentration of sulfate in sample, µg/mL

C_b = concentration of sulfate in blank, µg/mL

V_s = volume of sample, mL

K = milliequivalent volume, 11.2×10^3 µL

W_m = milliequivalent weight of sulfate, 48×10^3 µg/meq

V_m = volume of gas sampled, L

SULFUR DIOXIDE CONCENTRATIONS

In Manual Impinger Samples

The concentration of sulfur dioxide in manual impinger samples is calculated as follows:

$$C_{SO_2} = \frac{(V_t - V_b)N(\frac{V_s}{V_a})K}{V_m} \quad (5)$$

where

C_{SO_2} = concentration of SO_2, ppm by volume

V_t = volume of $Ba(ClO_4)_2$ used for the sample, mL

V_b = volume of $Ba(ClO_4)_2$ used for blank, mL

N = normality of $Ba(ClO_4)_2$, meq/mL

V_s = volume of sample, mL

V_a = volume of aliquot titrated, mL

K = milliequivalent volume, 11.2×10^3 μL

V_m = volume of gas sampled, L